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VOL. 32. No. 276. DECEMBER 1946.

REVIEW OF THE CHEMICAL STRUCTURE OF FUELS AND THEIR DETONATION IN ENGINE.

By A. G. MAZURKIEWICZ, A.M.I.Chem.E., and V. G. OBERHOLZER, B.A.

SUMMARY.

Due to the large accumulation of data published by the many laboratories working on the subject of combustion during the war, a need has arisen for a general review of the results.

An attempt has been made here to bring out the salient features of the methods of investigation employed in this field. Some general suggestions have been put forward for the different classes of compounds considered in an effort to correlate chemical structure with engine performance of fuel and fuel additives.

INTRODUCTION.

THE problem of the elimination of knock phenomena during the combustion of fuels in reciprocating engines has been the subject of close collaboration between those interested in the theory and processes of combustion and those more concerned with its practical application.

The process of combustion of hydrocarbons is, in itself, extremely complicated, and the investigation of the influence of given factors is often laborious. Even more difficult is the simulation of engine working conditions in the laboratory to give results applicable to full-scale engines. Laboratory methods mainly used in investigating processes of combustion have not as yet given any satisfactory or corresponding results.

The data for hydrocarbons, such as the values obtained for temperature of self-ignition, velocity of flame propagation, ignition-lag, and their dependence on temperature and pressure, give only a qualitative measure of the direction of the development of the combustion process in an engine. Consequently no absolute figures are obtained which could be, for instance, related to the octane number by a simple mathematical formula.

Due to the urgency of these problems, investigation of knock phenomena was studied in a test engine, giving results directly applicable to any engine, since the experimental conditions approximate closely to actual working conditions. This does not imply that the combustion process occurs under simplified conditions; on the contrary, the experimental conditions are even more complicated. The results obtained, however, could be applied with far greater assurance to a full-scale engine than those from other methods.

During the test of the knock properties of a fuel not only the fuel itself, but also the apparatus—in this case, the test-engine—and its operating conditions have a decisive influence upon the measured result. Therefore when citing the performance figures of a fuel one must necessarily mention the kind of test method applied. The great divergence in results sometimes obtained from measurements of the octane number of fuels is due in most cases to the different engine conditions under which measurements were made. Great care has therefore to be taken if the test data is to be applied to a full-scale engine.

Knock-rating.

Among the many engine-methods widely used in Great Britain and in America, two main groups may be distinguished:

(*a*) Critical compression ratio methods which have a variable compression ratio of the cylinder and a constant intake pressure;
(*b*) Supercharged methods which use a constant compression ratio but have a variable intake pressure and mixture composition.

To the group (*a*) belong the C.F.R. Research Method, C.F.R. Motor method and A.F.D. 1C method.[1] In the group (*b*) are the A.F.D. 3C Method.[2] American methods F-3 and F-4 and other individual methods used by different oil companies and other big firms such as: the 17·6 Method accepted by N.A.C.A. and Ethyl Gasoline Corpn.,[3] and original methods applied by General Motors [4] or I.G. Farbenindustrie [5] and B.M.W. in Germany.

This division of the methods into two main classes is very helpful when considering knock data and the relative performance of any two fuels.

It is a well-known fact that the preliminary reactions which develop in an air–fuel mixture during the compression stroke are responsible for the knock phenomena. They give rise to the formation of active knock-producing agents in such a quantity that, at the moment of increase of temperature up to a certain value, a very rapid oxidation in the whole mass occurs accompanied by the characteristic knock.

The temperature before the passing of a spark—*i.e.*, after the compression stroke—has a decisive influence upon the occurrence of the knock. It is dependent on the compression ratio in a given cylinder according to the usual formula for adiabatic compression:

$$T_2 = T_1 \cdot \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}.$$

Consequently, in the comparison of two fuels tested on the C.F.R. M.M. engine we have strictly speaking two variables for each fuel: the type of fuel and the critical compression ratio. We would therefore be comparing—and this is important—the knockings of two fuels which were obtained at different temperatures due to the different compression ratios. The better fuel is therefore tested under more unfavourable conditions. At a compression ratio of 8 or more the increase in temperature is so big that it obliterates the differences in the development of the preliminary reactions and just causes ignition to occur in the whole mass instantaneously. This explains the fact that the so-called "good fuels," such as Triptane or 100/150 fuel, which have a very high performance as compared with *iso*-octane on the A.F.D-3C engine, differ only slightly or not at all from pure *iso*-octane when tested on the C.F.R. M.M. Engine.

The AFD-1C method [9] especially takes into account the influence of temperature on the knock-phenomenon. The criterion of knock in this method is not the frequency of its occurrence as registered on a knock-meter, but the increase in temperature occurring under knock conditions. This increase is compared with the corresponding value of a reference fuel such as benzene, and 87 O.N. *iso*-octane and *n*-heptane blend.

In the measurement of anti-knock properties of a fuel in an engine the air-intake temperature is the most important factor in which only relatively small errors may be tolerated.[6, 7, 8] The marked influence of air-intake temperature (A.I.T.) on the knock performance of a fuel has been well confirmed. Certain hydrocarbons, such as aromatics, are very sensitive in this respect. Their low performance of the C.F.R. M.M. engine is due to the rapid decrease in their anti-knock properties with increase in the intake temperature (300° F. in C.F.R. M.M. method) and compression ratio.

Results obtained from the C.F.R. Motor method give no indication as to the behaviour of fuels at rich fuel–air mixtures or supercharged conditions, but just give a reasonable measure of the knock resistance of the fuel at lean fuel–air mixture—in other words, under cruising conditions.

The AFD-3C engine method seems to be more valuable than the earlier models because it determines the behaviour of fuel along the whole range of fuel–air mixtures. The compression ratio is constant at 7 : 1, hence the increase in temperature due to adiabatic compression is also constant for the mixtures of the same strength such as are usually compared.

The flame temperature of the progressing explosive wave depends on the composition of the mixture. The temperature of the combustion increases as the mixture composition approaches the stoichiometric proportion, and near this point the knock resistance of a fuel has its smallest value, therefore knocking will occur at lowest boost.

In the above outline emphasis has been laid on the importance of the influence of the test method upon the final result of fuel testing. The necessity of testing fuels over the whole range of mixture composition must be particularly stressed.

According to the opinion of N.A.C.A. or Ethyl Gasoline Corpn., AFD-3C Method (American F-4) is the most reliable method,[3] and it simulates the full-scale engine conditions with the best conformity.

As far as the fuel itself is concerned the purity of the sample to be tested must be assured. Samples of pure hydrocarbons are sometimes quite difficult to obtain, and this fact makes F-3 or F-4 tests of restricted applicability. This fact, together with the results of investigations carried out on the behaviour of fuel blends, has led to the use of " blending octane numbers " which will be dealt with later.

Knock Characteristics of Fuels.

The connection between the chemical structure and anti-knock properties has always attracted the attention of physical chemists. The character of the work requires a system of classification whereby compounds may be divided into definite groups and each group considered separately.

First considering hydrocarbons, paraffins, olefins (diolefins), acetylenes, naphthenes, and aromatic hydrocarbons, the relation between their molecular weights and boiling-points and their octane numbers is illustrated in Fig. 1.[9] This gives some comparison between the different groups of hydrocarbons having the same number of carbon atoms. Anti-

knock properties in general decrease with increasing molecular weight for normal paraffins, α-olefins, and naphthenes. Aromatic hydrocarbons, however, are quite the reverse, improving their anti-knock values with increasing molecular weight, whereas the *iso*-paraffin show little variation in this respect. In the paraffins and olefins chemical structure has the largest effect on the knock performance of the various isomers. The number of possible isomers, as in the paraffins, increases enormously with increase in number of carbon atoms. Thus butane has only two isomers, heptane-9, tridecane-802, and hexadecane about 10,000.

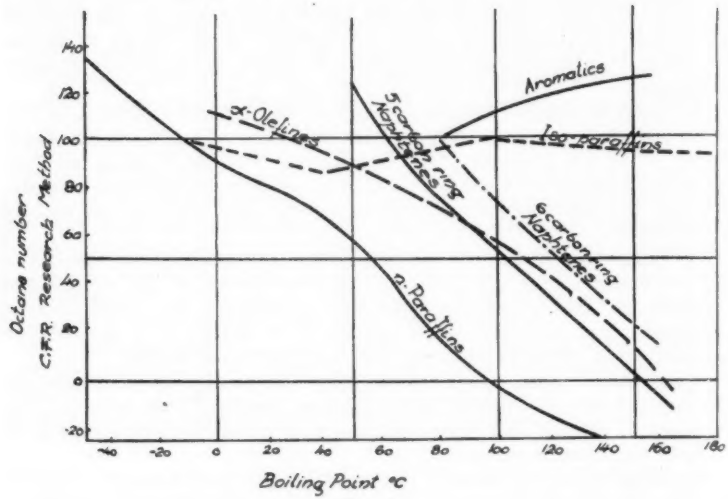


FIG. 1.

The *iso*-paraffins, which behave differently from the *n*-paraffins, generally have a great knock-resistance, and from a comparison between their chemical structure and octane values one can make the following general rules—the octane number rises with :

(1) Increased branching of hydrocarbon chain;
(2) Greater compactness of the branched structure;
(3) Increase in the symmetry of the structure.

These rules are observed for *iso*-paraffins in Table I.

The excellent anti-knock properties of 2 : 2 : 3-trimethylbutane and the effect of symmetry upon the knock performance in *iso*-paraffins attracted our attention to 2 : 2 : 3 : 3-tetramethylbutane. This compound we named "tetrane," from the analogy with triptane. Results of other investigators justified the hope that tetrane would prove outstanding as a fuel additive. Unfortunately it is a solid, and therefore its application would be largely governed by its solubility characteristics.

According to Fig. 1 olefins are better than the normal paraffins with

the same number of carbon atoms. The influence of branching is also considerable, and shown in Fig. 2.[4]

Thus we may deduce a further general rule that the presence of a double-bond is a favourable factor in chemical structure regarding the

TABLE I.

Octanes.

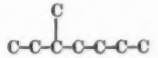
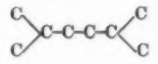
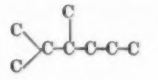
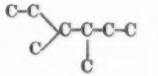
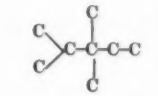
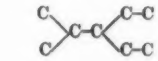
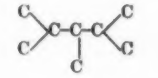
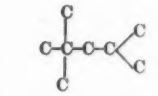
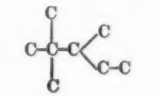
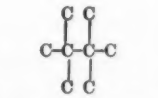
Chemical name.	Chemical structure.	C.F.R. M.M. octane number.
n-Octane		−17 [10]
3-Methylheptane		26·8 [11]
2 : 5-Dimethylhexane		55·8
2 : 3-Dimethylhexane		78·9
3 : 4-Dimethylhexane		81·7
2 : 3 : 3-Trimethylpentane		99·4
2-Methyl-3-Ethylpentane		88·1
2 : 3 : 4-Trimethylpentane		95·9
2 : 2 : 4-Trimethylpentane		100
2 : 2 : 3-Trimethylpentane		99·9
2 : 2 : 3 : 3-Tetramethylbutane [12]		103

TABLE II.[12]

Blending Octane Numbers of iso-*Paraffins* (*C.F.R. Research Method*).

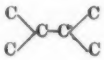
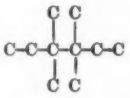
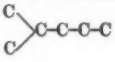
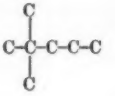
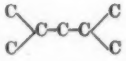
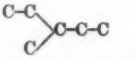
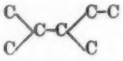
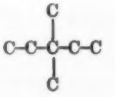
Hydrocarbon.	Chemical structure.	Octane number.
Tetramethylmethane		116
2 : 3-Dimethylbutane		124
2 : 2 : 3-Trimethylbutane (triptane) .		116
2 : 2 : 3 : 3-Tetramethylbutane (tetrane)		130
3 : 3 : 4 : 4-Tetramethylhexane . .		124

TABLE III.[12]

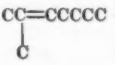
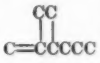
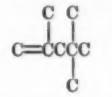
Symmetry and Blending Octane Number (*C.F.R. Research Method*).

Hydrocarbon.	Chemical structure.	Octane number.
2-Methylpentane		69
2 : 2-Dimethylpentane		80
2 : 4-Dimethylpentane		80
3-Methylpentane		84
2 : 3-Dimethylpentane		94
3 : 3-Dimethylpentane		98

knock performance. The position of the double bond is also an important factor, being more favourable when nearer the "centre" of the compound, and the diolefins are greatly improved if their double bonds are conjugated. The general rules given above in the case of *iso*-paraffins can be applied successfully to *iso*-olefins, as seen in Table IV.

TABLE IV.[11]

Properties of iso-*Olefins.*

Hydrocarbon.	Chemical structure.	Octane numbers.	
		C.F.R. Res.M. 212° F A.I.T.	C.F.R. M.M. 300° F A.I.T.
3-Octene	CCC=CCCCC	72·5	68·1
2-Methyl-2-heptene . . .		75·9	71·0
2 : 3-Dimethyl-1-hexene . .		96·3	83·6
2 : 4 : 4-Trimethyl-1-pentene .		100 + 0·5	88·6

It is quite difficult to establish a general rule regarding naphthenes either for the 5- or 6-ring compounds. Their octane values lie in between

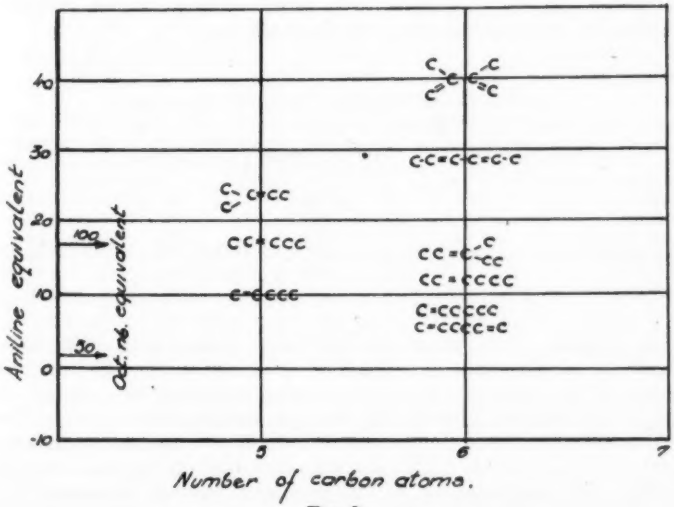


FIG. 2.

those for the *n*-paraffins and aromatics with the same number of carbon atoms. One may safely assume that such values give a measure of the influence of the saturated rings, since the number of C and H atoms is identical with that of the corresponding olefins and there are no double bonds present. The effect of a saturated six-carbon ring thus seems to have a stronger influence than the double bond in olefinic compounds. The octane value of naphthenes decreases with increase of molecular weight, especially when the side-chains are *n*-alkyl-groups. The presence of branched (*iso-* or *tertiary-*) alkyl groups in side-chains improves the performance appreciably, as also does the presence of a double bond in the ring.

Aromatic hydrocarbons constitute a chemical group combining both unsaturation and a 6-carbon atom ring. Such a combination is, as one would expect from the above, very good, and in fact aromatics are excellent anti-knock compounds. Molecular weight increase at low air-intake temperatures has here the reverse effect to that given by the previous groups considered. This is shown in Fig. 1, which was constructed from data obtained using the C.F.R. Research Method where air-intake temperature is 212° F and engine speed 600 r.p.m.

The first three homologues of the aromatic series under C.F.R. M.M. conditions—*i.e.*, at higher intake temperature 300° F and engine speed 900 r.p.m.—show the reverse sequence, the critical compression ratios having the following values:

Xylene	10·8
Toluene	11·5
Benzene	12·6

Benzene here has the highest C.C.R.,[14] in that as the air-intake temperature increases the anti-knock properties decrease for all three, but to a different degree. Xylene is the most sensitive to an increase of temperature, whereas benzene is the least affected.

TABLE V.[15]

Blending Octane Numbers of Aromatic Hydrocarbons.

Hydrocarbons.	C.F.R. Res.M.	C.F.R. M.M.	Drop in octane number.
Benzene	108	87	21
Toluene	120	90	30
Ethyl benzene	128	97	31
o-Xylene	121	97	24
m-Xylene	144	104	40
p-Xylene	154	104	50

The increase of air-intake temperature in the C.F.R. M.M. severely affects the performance of aromatics, whereas in the AFD-3C rating method all the advantages of the aromatics can be shown. Other supercharged test methods give similar results in this respect.

Tests were conducted in a Wright R-1820 G200 cylinder at cruise rating (2000 r.p.m. and 210° F A.I.T) and take-off rating (2500 r.p.m. and 250° F A.I.T). The concentration of the aromatics were 25 per cent. vol. in the reference fuel 85 O.N : C.R. 7·3 : 1; Spark advance 20° B.T.C.[16]

Each compound gives two values, a lower and higher one, under operating conditions, as indicated :

TABLE VI.

Hydrocarbon.	% Knock limited I.M.E.P. of *iso*-octane.
Benzene	93–123
Toluene	112–149
p-Xylene	121–164
Mesitylene	125–172

The sequence of knock values is in full conformity with the results obtained in the C.F.R. Research Method. As mentioned before, the influence of temperature in the supercharged methods is contained in the specific fuel consumption or fuel–air ratio. The closer the fuel–air mixture is to the stoichiometric composition the higher the temperature of combustion becomes. Fig. 3 shows the steep fall of the rating curve of an aromatic fuel when tested at lean mixtures—*i.e.*, at higher temperatures.

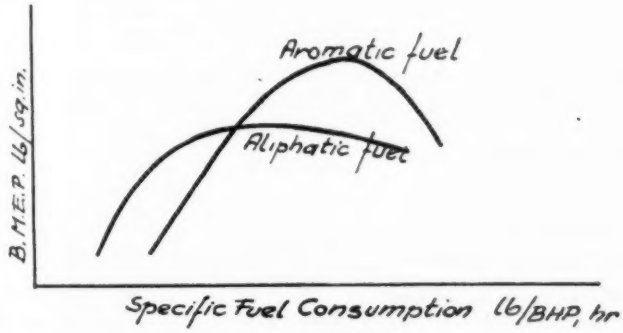


FIG. 3.[17]

The paraffins or the naphthenes never show quite the same sensitivity to increase in air-intake temperature.

Side-chains in aromatic compounds have a similar effect to those in the naphthene group. Very long, unbranched chains do not have any favourable influence, whereas short and strongly branched chains improve the performance noticeably.

This influence of branched side-chains appears repeatedly in all kinds of hydrocarbons, those found as components in crude oil and those synthetically produced.

Aliphatic alcohols and ketones show a similar behaviour with regard to the structure of their side-chains, their length, and grade of branching. These points are illustrated in Tables VII and VIII.

TABLE VII.[4]

Alcohol.	Structure.	Aniline number.
n-Heptanol	CCCCCCC–OH	−6
1-Methylhexanol . . .	CCCCCC(–OH)(C)	2
1-Propylbutanol . . .	CCCC(–OH)(C)C(C)C	9
1-*tert.*-Butylpropanol . .	CCC(–OH)(CCC)C	13
2 : 2 : 3 : 3-Tetramethylpropanol	CC(CC)(CC(O)(CC)CC)CC	21

TABLE VIII.

Ketone.	Structure.	Aniline number.
Methyl-*n*-hexylketone . .	CCCCCCC(=O)C	−1
Di-*n*-propylketone . . .	CCC–C(=O)–CCC	5·5
1 : 3-Pentadione (acetylacetone)	CC(=O)CC(=O)C	15

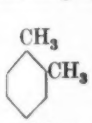
The most favourable positions are the *para*-, then the *meta*-, and lastly the *ortho*-, the effect of which is sometimes negative—*i.e.*, knock promoting.

Two xylenes were tested under conditions mentioned in Table V giving the following ratings:

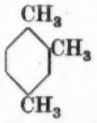
p-Xylene . . . 121–164
o-Xylene . . . 71– 99 } per cent. I.M.E.P. of *iso*-octane.

The reference fuel was a 85 O.N. fuel, and the concentration of the test fuel in the reference fuel was 25 per cent vol. The figures obtained from a supercharged method confirm the results given in Table V. *o*-Xylene decreases the octane number, when tested in weak mixtures, down to 71, thus acting as a knock promoter, and this was in good agreement with results of other workers.[18]

Among the trimethyl benzenes 1 : 3 : 5-compound (mesitylene) has a better performance than 1 : 2 : 4-compound (pseudo-cumene).[19] The values obtained under conditions given in Table V are for mesitylene 127–172, and for pseudo-cumene 87–110. Comparing these with similar values for *ortho-* and *meta*-xylenes we may conclude that the influence of *ortho*-alkyl groups is unfavourable when compared with the *para*-groupings. Such conclusions fall in line with the general rule of symmetry, especially in view of the good performance of mesitylene (*sym.*-trimethylbenzene), where we have *meta*-groupings. This is better seen from the following figures :

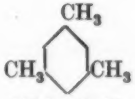


o-Xylene 71–99.



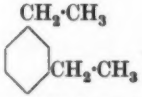
1 : 2 : 4-Trimethylbenzene (pseudo-cumene) 87–110.

p-Xylene 121–164.

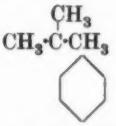


1 : 3 : 5-Trimethylbenzene (mesitylene) 127–172.

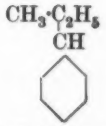
Similar figures for other alkyl groupings with their respective structures are :—



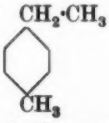
m-Diethylbenzene 141–171.



t-Butylbenzene 130–155.



sec.-Butylbenzene 111–138.



1-Ethyl-4-methyl benzene 118–166.

*iso*Propylbenzene 127–148.

In the alkyl benzenes one can conclude that better results will be obtained if the alkyl groups are more highly branched and that there are 2 or 3 substituted in either *meta-* or *para*-positions to each other.

A double bond in the side-chain also has a favourable effect, especially when conjugated relative to those in the benzene ring, as evidenced by the values in Table IX.

The aromatic amines must be considered as a separate group, due to their high performance figures and their wide application during the war.

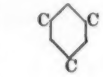
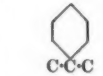
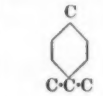
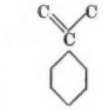
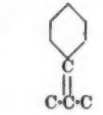
As a rule, these amines increase the anti-knock resistance only within the range of rich mixtures, although some of them are quite satisfactory in weak mixtures.

From the exhaustive work done on amines and the figures published one may draw certain general conclusions.

The presence of NH-groups is of prominent importance, and aryl-NH groupings are far better than the alkyl-NH groups. The lowest per-

TABLE IX.

Blending Octane Numbers C.R.F. M.M.

Hydrocarbon.	Structure.	Blending octane number.
p-Xylene		127
Mesitylene		137
iso-Propylbenzene . . .		124
1-Methyl-4-*iso*-propylbenzene . .		133
2-Phenylpropene		150
1-Phenyl-2-methylpropene . .		136
1-Methyl-4-allyl-1-benzene . .		134

formance in this respect is obtained when all the three N-valencies are substituted by radicals.[20]

The homologues of aniline follow a similar sequence to the other aromatic compounds and also obey the same general rules concerning *ortho-* and *para*-positions, as indicated in Table X.

It is evident that the best positions for the alkyl groups are *para-* to the N-atom and worst when they are in the *ortho*-position.

The substituted diphenylamines such as the ditolylamines were investigated in the hope that the good results obtained in the rating of diphenylamine,[22] and the limited solubility in gasoline, especially at low temperatures,[23] would be improved. The results as given in Table XI do not fulfil this hope.

TABLE X.[21]

Compound.	% vol.	Structure.	3-C Rating equal to *iso*-octane + c.c. T.E.L./gal.
Aniline	1		1·2
o-Toluidine . . .	1		1·1
m-Toluidine . . .	1		1·3
p-Toluidine . . .	1		1·5
2 : 3-Xylidine . . .	3		2·6
2 : 4-Xylidine . . .	3		4·1
2 : 5-Xylidine . . .	3		4·3
2 : 6-Xylidine . . .	3		2·7
3 : 5-Xylidine . . .	3		3·4
3 : 4-Xylidine . . .	3		6·1
o-Ethylaniline . . .	3		1·4
p-Ethylaniline . . .	3		5·8

TABLE X—(*continued*).

Compound.	% vol.	Structure.	3-C Rating equal to *iso*-octane + c.c T.E.L./gal.
3 : 4 : 5-Trimethylaniline .	3		4·2 (extrapolated)
2 : 4 : 6-Trimethylaniline .	3		3·1

TABLE XI.

Compound.	% W/W in blend.	Increase in octane number (C.F.R. M.M.).
Diphenylamine . . .	2	6·0
m-Ditolylamine . . .	2	3·5
p-Ditolylamine . . .	2	5·6

The reference fuel was a 72 O.N. (C.F.R. M.M.) fuel. The favourable influence of the *para*-positions compared to the *meta*- are here apparent. Unfortunately the results are not of practical importance, in that the only great increase in solubility is given by the *meta*-compound, which, unlike the others, is a liquid at ordinary temperatures.

The substitution of all the N-valencies gives a very meagre effect if not a negative one in the weak mixture region. This can be seen from the ratings of such compounds as dimethylaniline and diphenylaniline when tested in the C.F.R. Motor and a full-scale engine.[24]

The presence of a nitroso-group causes a drop in the performance of amines. Diethyl aniline and *p*-nitrosodiethylaniline are compared in Fig. 4.

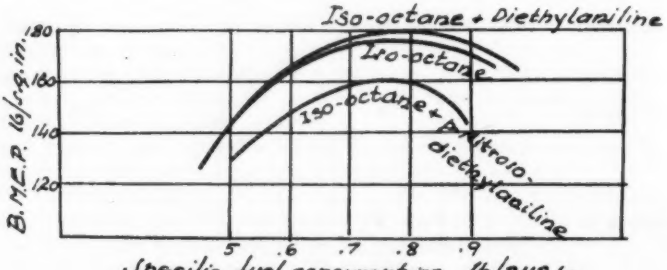


FIG. 4.

This diagram indicates the negative influence of the NO group, which acts as a knock promoter, and in fact it makes little difference if the NO is chemically combined, as in the above amine, or added separately.

The blending effect must be taken into account when separate groups of hydrocarbons are being compared. When two hydrocarbons of different octane value form a blend the resulting octane value will not always obey the mixing rule. This applies to paraffinic and *iso*-paraffinic hydrocarbons which give the blending octane number according to the reciprocal blending equation when tested under supercharged conditions.[25]

The mathematical expression for the blending value obtained from a C.F.R. method is far more elaborate.[26] All such equations enable the blending octane number of a compound to be anticipated when its performance in a blend with a reference fuel is known.

Olefins and aromatics behave in different ways. The former when applied in the usual percentages raise the octane value according to a certain blending factor. Further increase in the proportion of olefins present does not raise the octane value proportionally, but to a much smaller degree. The behaviour of aromatics is just the opposite. Small additions increase the performance much less proportionally than do larger quantities in a given reference fuel. Fig. 5,[27] which illustrates the behaviour of three groups of hydrocarbons—*i.e.*, paraffins, olefins, and aromatics, gives only an approximate and simplified picture of their blending octane numbers against their concentration in the blends.

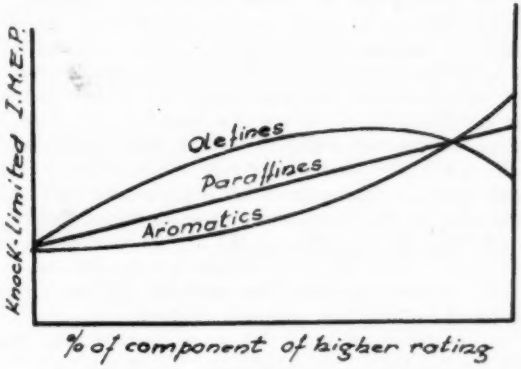


FIG. 5.

More accurate data on blending octane numbers have been published by Garner and co-workers, and they show the relation between concentration and octane number in an exhaustive manner.[32] They include also the behaviour of naphthenes, which is almost similar to that of paraffins, except the different behaviour of pure *cyclo*-hexane—*i.e.*, the high blending effect at low concentrations.

Discussion of Results.

The numerous factors which influence the combustion of a fuel in an engine make it impossible to give any simple picture of the whole combustion process. An intricate series of changes occur with each stroke in a reciprocating engine; thus, there appears to be low temperature oxidation with cool flame phenomenon, normal spark ignition, and travelling flame or spontaneous ignition, and finally simultaneous oxidation in the whole mass—*i.e.*, knock.

Such aspects can hardly be attributed wholly to the physical and thermodynamical conditions accompanying the process, such as temperature, pressure, surface-development, and its relationship to the volume.

The fuel as a chemical individual, including all anti-knock additives, has also a decisive influence on the process of combustion. Thus lead tetraethyl, although having no effect on the velocity of flame propagation, is the most prominent knock suppressor.[28]

The production of free radicals and their further development are responsible for the progress of the chain reaction of oxidation. The free radicals under given physical and thermodynamical conditions are formed and destroyed at the same time. The resultant of these two opposing tendencies—*i.e.*, a measure of the quantity of free radicals available at any given time—gives rise to the so-called ignition lag.

Fuels of certain chemical types, instead of undergoing degradation through the separate stages of oxidation with simultaneous cracking,[29] form by branch reactions a large number of free radicals, which, when the temperature conditions are fulfilled—by the approach of the high-temperature flame front—produce explosion in the whole mass. The time necessary for the formation of such a quantity of free radicals is most probably the ignition delay. When the time for complete combustion is smaller than the ignition delay under the given conditions, the combustion occurs normally—otherwise knock occurs before the flame front has sufficiently spread. These times can be influenced by physical factors such as shortening of the flame path, speeding up of flame-propagation by turbulent motion, development of the surface, and changing temperature and pressure. The occurrence of knock may also be influenced in a chemical way by the removal of free radicals and chain carriers—viz., by the addition of suitable fuel and fuel additives.

The different behaviour of hydrocarbons in their tendency to "knock" can be attributed to their susceptibility to "oxygen attack." According to Walsh,[30] a tertiary $CH\lessdot$ group is attacked before other hydrocarbon groupings, forming peroxides quite readily. These peroxides decompose quickly to give lower peroxides, and finally ketones are produced; the low-temperature chain reactions then stop. The secondary $CH_2=$ group forms a peroxide more easily than the primary CH_3- group; the peroxide breaks down finally into a lower aldehyde and water.

This scheme accounts for the good performance of highly branched paraffins, which all give ketones as the final product of the initial degradation. Where aldehydes (especially formaldehyde) are formed as the main products the fuel has a low performance. Even straight-chain

compounds, if they give ketones, are good fuels, as in case of *iso*-propyl alcohol. The presence of double bonds is also favourable for removal of free radicals hence the good anti-knock properties of olefins and aromatics.

In general, therefore, better results will be obtained when only a limited quantity of radicals are produced ($PbEt_4$ acts as a knock promoter at high concs.[31]), when branched radicals are produced which easily break down through the peroxide into ketones and when in general ketones are formed and only a limited amount of formaldehyde.

These considerations give only a very rough indication of the chemical factors influencing combustion. The influence of additives as knock promoters or suppressors is probably limited by their effect on the ignition lag, which consequently has its influence on the completion of the normal combustion without detonation.

This review it is hoped will be supplemented in the future by consideration of the influence of radicals such as triphenyl methyl, of the effect of double bond in aromatic side-chains and of the applicability of bromo fuels in an effort to replace ethylene dibromide in leaded fuels.

The authors wish to express their thanks to Dr. G. W. S. Parker for his interest and advice during this work.

Royal Aircraft Establishment,
January 1946.

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THE VAPORIZATION OF FUELS FOR GAS TURBINES. PART I. THE BUBBLE-POINTS AND DEW-POINTS OF LIQUID HYDROCARBON FUELS.

By B. P. Mullins.

Summary.

The search for new and improved forms of gas-turbine combustion chambers naturally turns towards systems with perfect fuel atomization, an ideal that can be realized by pre-vaporization of the fuel. The evaluation of the vaporization characteristics of gas turbine fuels described in this paper is the first step towards achieving this ideal.

A review of the empirical methods devised during the past twenty-five years for determining the bubble-points and dew-points of liquid hydrocarbon fuels is given, and these are applied to standard fuels. Some practical determinations involving the preparation of "equilibrium solutions" by the method of Wilson and Barnard [1] were also undertaken. Finally a theoretical method for calculating bubble-points and dew-points, depending on a knowledge of the true boiling-point distillation curve of the fuel in question was developed and applied to standard fuels.

The calculations cover a static pressure range of 10^{-2} to 10 atmospheres and have been extended to air–fuel ratios of 0 : 1 to 20 : 1. The main results for an aviation spirit, a kerosine, and a gas oil are presented in the form of nomograms.

List of Symbols.

Notation.

e = base of natural logarithms.
G = Gruse's index-number.
K_1, K_2 = constants.
L = latent heat of vaporization.
m = mass.
M = molecular weight.
$\bar{M}$ = mean molecular weight.
n = an integer.
p = partial pressure.
P = vapour pressure.
π = total (externa lor static) pressure.
R = air/fuel ratio (by weight).
R' = gas constant.
S = slope of A.S.T.M. distillation curve.
t = temperature.
V = volume (of gas or vapour).
v = volume (of liquid).
x = molar fraction in liquid phase.
y = molar fraction in vapour phase.

Suffices.

A, B, C refer(s) to components A, B, C.
1, 2, 3 ,, components 1, 2, 3.
a ,, air.
f ,, fuel.
i_0 ,, component i in the original liquid fuel.
i ,, component i in the liquid phase.
i' ,, component i in the vapour phase.
B ,, the bubble-point if accompanied by a lower suffix, otherwise the boiling-point. (Sometimes occurs as a suffix in a superscript).
NB ,, the normal boiling-point.
EAD ,, the equilibrium air distillation (temperature).
D ,, the dew-point. (Sometimes occurs as a suffix in a superscript.)
ND ,, the normal dew-point.
q ,, the A.S.T.M. distillation q per cent point. (Any equation containing t_q automatically refers to atmospheric pressure; sometimes written merely as a number.)

Lower Suffix.

R refers to an air/fuel ratio of $R:1$ (usually written merely as a number).

Superscripts.

q refers to the A.S.T.M. distillation q per cent point.
t „ temperature t, (sometimes written merely as a number).

Summation Limits.

$1 \ldots n$ refer to the n components of a fuel.
$1 \ldots n^1$ „ n^1 components of air.

1. Introduction.

The work on the vaporization of gas turbine fuels has been conveniently separated into two parts as follows:—

Part I. The bubble-points and dew-points of liquid hydrocarbon fuels.

Part II. Heat quantities required to vaporize gas-turbine fuels.

The present paper deals with Part I of this programme, and for this work a standard Air Ministry 100-octane fuel, a standard kerosine (burning oil), and a typical gas oil were chosen, although the method of calculation developed is sufficiently general to be applicable to other possible gas-turbine fuels.

Definitions of several terms relating to hydrocarbon mixtures will first be given:

Definition 1. *Bubble-Point* ($R:1$). The bubble-point ($R:1$) of a hydrocarbon fuel is the temperature at which equilibrium exists between the wholly condensed fuel and an infinitesimal quantity of its vapour mixed with air in the ratio 1 to R.

Definition 2. *Dew-Point* ($R:1$). The dew-point ($R:1$) of a hydrocarbon fuel is the temperature at which equilibrium exists between the wholly vaporized fuel plus air mixed in the ratio 1 to R, and an infinitesimal quantity of the liquid fuel.

Definition 3. *Component.* A narrow boiling-range cut of a liquid hydrocarbon fuel, as well as a pure hydrocarbon, are defined here by the word "component."

It should be noted that the composition of the infinitesimal quantity of vapour referred to in Defn. 1 and of liquid in Defn. 2, while being related to the composition of the fuel, are not identical with it.

There are five distinct types of equilibrium possible in fuel–air mixtures, where the fuel consists of a mixture of hydrocarbons and possesses a boiling range. They are all special cases of the one general equilibrium condition where x per cent of the fuel is evaporated and is mixed with air in the ratio $R:1$ by weight, whilst the remaining $(100 - x)$ per cent is in immediate contact with this vapour. The five conditions are set out in Table I.

The *boiling-point* of a fuel is equal to the bubble-point when the air–fuel ratio is zero—*i.e.*, t_{NB}.

The *normal boiling-point* of a fuel is equal to the boiling-point under an external pressure of 1 atmosphere.

TABLE I.

Possible Equilibrium Conditions between Fuel and Air Mixtures.

There are five distinct types of equilibrium possible in fuel–air mixtures, where the fuel consists of a mixture of hydrocarbons and possesses a boiling range. They are all special cases of the one general equilibrium condition where x per cent of the fuel is evaporated and is mixed with air in the ratio R to 1 by weight, whilst the remaining $(100 - x)$ per cent is in immediate contact with this vapour mixture. The five conditions are tabulated below.

Name.	Symbol.	Fuel evaporated, %.	Air–fuel ratio.	Nature of the two phases.	
				Vapour phase.	Liquid. phase.
Normal bubble point	NB	0	0	Fuel (infinitesimal)	Fuel
Bubble point	B_R	0	R $(0<R<\infty)$	Fuel (infinitesimal) + Air (infinitesimal)	Fuel
Equilibrium air distillation point	$EAD_R{}^x$	x $(0<x<100)$	R $(0<R<\infty)$	Air and Fuel	Fuel
Dew-point	D_R	100	R $(0<R<\infty)$	Air and Fuel	Fuel (infinitesimal)
Normal dew-point	ND	100	0	Fuel	Fuel (infinitesimal)

All these equilibria may be defined at pressures other than 760 mm mercury, and the temperatures corresponding to the various equilibria fall in the following ascending order for a given R (R small) :—

$$t_{B_R} < t_{NB} < t_{EAD_R} < t_{D_R} < t_{ND}$$

This would be expected from the fact that as we pass through the five equilibrium conditions in the order indicated by these temperatures the molecular weight of the vapour increases from that of air to that of fuel.

If R be very large it is possible that $t_{NB} > t_{D_R}$ and the inequality must be expressed in two parts thus :—

$$t_{B_R} < t_{EAD_R} < t_{D_R} \text{ and } t_{NB} < t_{ND}$$

It will be found that for any given R whatsoever

$$t_{EAD_R{}^{x_1}} < t_{EAD_R{}^{x_2}},\ (x_1 < x_2).$$

2. EMPIRICAL METHODS.

2.1. *Description of Methods.*

Many useful empirical volatility relations for motor fuels and aviation spirits have been developed by Bridgman,[2-7] who based his work upon the A.S.T.M. distillation curves [8] of these fuels. He represented the volatility of a fuel by the temperature at which a given air–vapour mixture will be formed under equilibrium conditions at a pressure of one atmosphere from any mixture of liquid fuel and air supplied, when a given percentage was evaporated. The temperatures at 0 per cent evaporated are called "bubble-points" at 100 per cent evaporated "dew-points," and at intermediate percentages evaporated "equilibrium-air-distillation" (E.A.D.) points. The bubble-points may be obtained from the curve representing

any given air–vapour mixture by extrapolating back to the line of 0 per cent evaporated. The normal bubble-point is the temperature at which bubbles will start to form in a gas-free fuel at atmospheric pressure, and corresponds to the boiling-point. Bridgman found that :—

$$t_{NB} = t_{10} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

within the accuracy of determining the latter, for ten gasolines of widely differing types. (Temperatures are to be expressed in ° C unless otherwise stated.)

$$\log_{10} P = 6{\cdot}76 - 3{\cdot}88 t_{NB}/t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

for gasolines freed from water and dissolved gases, but without removal of propane or any of the more complex hydrocarbons. The temperatures in equation 2 must be expressed in degrees Kelvin.

$$t_{10}/t_{B16} = 1{\cdot}5 + (10\sqrt{S_{10}} - 39)/t_{B16} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$t_q/t_{EADq^q} = 1{\cdot}5 - \sqrt{(460\, S_q)} \log [(100 - q)/50] + 39 \quad . \quad (4)$$

where $10 \leqslant q \leqslant 90$.

$$t_{90}/t_{D16} = 1{\cdot}5 + (10\sqrt{S_{90}} - 39)/t_{D16} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

These results may be extended to temperatures other than the 16 : 1 temperatures by the following correction table :—

A/F Ratio.	Δt ° C.	A/F Ratio.	Δt ° C.	A/F Ratio.	Δt ° C.
8	+13	12	+5	17	−1
9	+11	13	+3½	18	−2
10	+ 9	14	+2½	19	−3
11	+ 7	15	+1	20	−4

$$t_{ND} \doteqdot t_{90}/1{\cdot}084 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$t_{D12} = t_{90}/1{\cdot}399 - 131 \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$t_{EAD12^q} = \tfrac{3}{5}(t_q - 200) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The temperatures in equations 7 and 8 are to be expressed in ° F, and q in equation 8 lies in the interval $10 \leqslant q \leqslant 90$.

As early as in 1921, Wilson and Barnard [1, 9, 10] recognized that if it were possible to secure any considerable quantity of that fraction which first condenses out from (and hence is in equilibrium with) the completely vaporized mixture, measurements of its vapour pressure would obviously give the dew-points at different pressures. To obtain a quantity of this equilibrium solution the test fuel was distilled under continuous equilibrium vaporization conditions. Continuous equilibrium vaporization may be defined as a distillation process in which the fuel is partly vaporized under such conditions that equilibrium exists between all the vapour formed and all the remaining liquid. The requirement of continuity of operation

presupposes an input of constant composition supplied at a constant rate, from which vapour and liquid of constant compositions and amounts are formed and continuously withdrawn. The apparatus used for this purpose is very simple (Fig. 4), and will be described in para. 3.1 below. Wilson and Barnard established several special curves from which the bubble-points, E.A.D. points, and dew-points of a fuel could be deduced: the vapour-pressure curves of the fuel and its equilibrium solution were needed for the construction of these special curves. A very rough relation for gasolines and kerosines is expressed by the following equation:—

$$t_{D_{13}} \doteqdot t_{85} - 135 \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Stevenson and Babor [11] in 1927 measured normal dew-points with a black surface dew indicator and then developed empirical curves from which the dew-points of different air–gasoline mixtures could be deduced. They found that this "equilibrium end-point" or dew-point of the gasoline alone was easy to determine, and that its relation to the dew-points of air–gasoline mixtures was sufficiently accurate for the derivation of the latter to be made by means of a graph, with practical accuracy. In this way one simple determination of the dew-point of gasoline alone sufficed for the deduction of the temperatures of complete vaporization of all the practical air–gasoline mixtures. The authors, in common with many others, expressed the view that the A.S.T.M. distillation curve and end-point do not express the total volatility of a gasoline, but that the equilibrium end-point (dew-point) represents by means of a single number this total volatility. Furthermore, it was contended that the order of relative volatility that exists at 760 mm pressure is the same as at 15 mm pressure, and that even the quantitative differences are proportionately maintained with approximate accuracy.

These conclusions were reached in spite of Gruses' earlier attempts [12, 13, 14] to derive a volatility index by weighting parts of the A.S.T.M. distillation curve. For a number of commercial gasolines Gruse found that an index-number could be calculated from the A.S.T.M. curve, which bore a linear relationship to the dew-points of the gasoline used. The index-number, G, was computed by taking the sum of the 10, 20, 50, 70, 90 per cent and end-points, and the following empirical relations were found to hold to within 5 to 10° C:—

$$t_{D_{15}} = [12 + 0{\cdot}187\ (G - 600)] \quad . \quad . \quad . \quad . \quad . \quad (10)$$

for gasolines with $612 < G < 1025$.

$$t_{D_{15}} = [10 + 0{\cdot}83(t_{85} - 115)] \quad . \quad . \quad . \quad . \quad . \quad (11)$$

for gasolines with $115 < t_{85} < 210$.

A chart based upon the Deppé end-point of the particular gasoline under test has been constructed by Stevenson and Stark [15], from which the dew-point of any air–gasoline mixture may be obtained to within ±2° C.

An empirical dew-point equation very similar to equation 7 was proposed by Brown [16, 17] which gave values generally 2° F lower than Bridgman's,

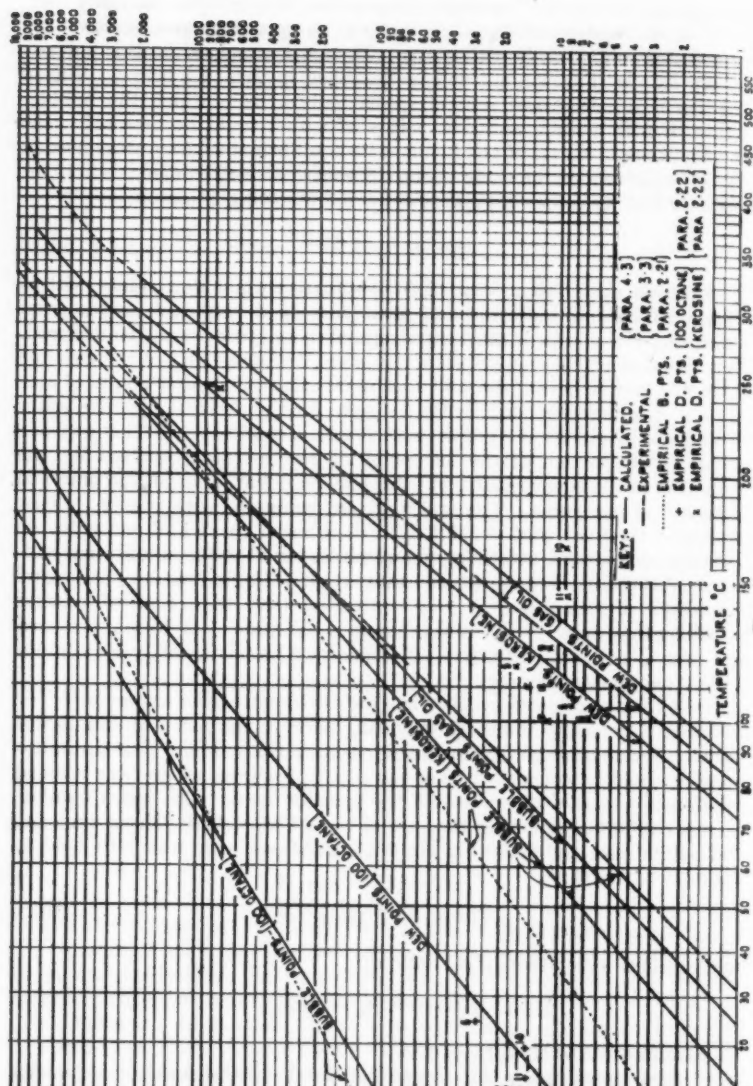


FIG. 1.

BUBBLE-POINT AND DEW-POINT CURVES FOR 100 OCTANE FUEL, KEROSINE AND GAS OIL.

It is :—

$$t_{D_{12}} = \frac{5}{7}(t_{90} - 186) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where the temperatures are in ° F. This equation is claimed to be accurate to within $\pm 5°$ F, except for highly aromatic fuels.

Brown and Skinner [16, 18] have investigated the effect of motor-fuel volatility as indicated by the A.S.T.M. distillation curve, upon engine performance. Their general conclusions are that the 90 per cent point should not be so low as to indicate a dry mixture, for this gives rise to loss of power or acceleration with many engines equipped with heated manifolds and accelerating devices : nor should the 10 per cent point be so low as to indicate trouble from vapour-lock. This indicates the engine evidence that the dew-point and boiling-point of a fuel are mainly functions of those hydrocarbon fractions boiling around the 90 and 10 per cent A.S.T.M. points, respectively.

Rules and formulæ have recently been derived by Aubert [19] giving the saturated vapour-pressure of liquid fuels as a function of the temperature.

2.2. *Results for* 100-*Octane Fuel and Kerosine.*

2.21. *Boiling-Points.* Bridgman's equations 1 and 2 were based on his work on gasolines; equation 2 has, however, been applied here to 100-octane fuel and kerosine, assuming the value of t_{NB} to be that computed under para. 4 below. The values obtained in this manner have been plotted as dotted lines in Fig. 1.

It is seen that agreement between the empirical and calculated values of boiling-point at the various pressures is better in the case of the 100-octane fuel than for the kerosine. The slopes of the empirical vapour-pressure lines are less than the slopes of the corresponding lines calculated from the true boiling-point distillation curves.

2.22. *Dew-Points.* The empirical dew-point equations given in para. 2.1 all express the dew-point of some air/fuel mixture in terms of certain properties of the fuel in question, with the exception of equation 6, which gives the normal dew-point. In order to compare the values graphically with the calculated values under para. 4, therefore, they have been converted into dew-points at some pressure other than 760 mm Hg for an air/fuel ratio of 0 : 1. This pressure is in fact the partial pressure of the fuel, and was obtained from the equations developed in para. 4 below. The values obtained in this way are plotted in Fig. 1, whilst the numeral written above each point is that of the empirical equation from which the value is calculated.

The set of dew-point values obtained by direct use of equations 5, 6, 7, 9, 10, 11, and 12 are set out in Table II.

For 100-octane fuel the agreement between empirically and theoretically calculated values is very close indeed, except for the very approximate equation 9 devised by Wilson and Barnard. For kerosine, the empirical equations 7, 10, and 11, which were developed for use in the gasoline range, give useless results; agreement between the other empirical and the theoretical values however is quite good.

FIG. 1. BUBBLE-POINT AND DEW-POINT CURVES FOR 100 OCTANE FUEL, KEROSINE AND GAS OIL.

TABLE II.

Results of Empirical Calculations on Reference Kerosine and 100-Octane Fuel.

(The corresponding values calculated under para. 4 are juxtaposed for comparison.)

Fuel.	Empirical.		Theoretical.	
	Para. 2.1 Equation No.	Dew-point values obtained, ° C.	Corresponding values obtained under para. 4, ° C.	Difference between empirical value and theoretical value, ° C.
100-octane	5	$t_{D_5} = 23\frac{1}{2}$	29	$-5\frac{1}{2}$
	5	$t_{D_{10}} = 10\frac{1}{2}$	16	$-5\frac{1}{2}$
	5	$t_{D_{50}} = 6\frac{1}{2}$	12	$-5\frac{1}{2}$
	6	$t_{ND} = 115$	108	$+7$
	7	$t_{D_{10}} = 11$	22	-11
	9	$t_{D_{10}} = -16$	22	-38
	10	$t_{D_{10}} = 19\frac{1}{2}$	18	$+1\frac{1}{2}$
	11	$t_{D_{15}} = 13$	18	-5
	12	$t_{D_{10}} = 10$	22	-12
Ref. kerosine	5	$t_{D_5} = 118$	126	-8
	5	$t_{D_{10}} = 105$	110	-5
	5	$t_{D_{50}} = 101$	107	-6
	6	$t_{ND} = 246$	239	$+7$
	7	$t_{D_{10}} = 100$	118	-18
	9	$t_{D_{10}} = 124$	118	$+6$
	10	$t_{D_{10}} = 155$	112	$+43$
	11	$t_{D_{15}} = 136$	112	$+24$
	12	$t_{D_{10}} = 112$	118	-6

The A.S.T.M. (I.P.T.) distillation curves and differential distillation curves for 100-octane fuel and kerosine are given in Figs. 2 and 3.

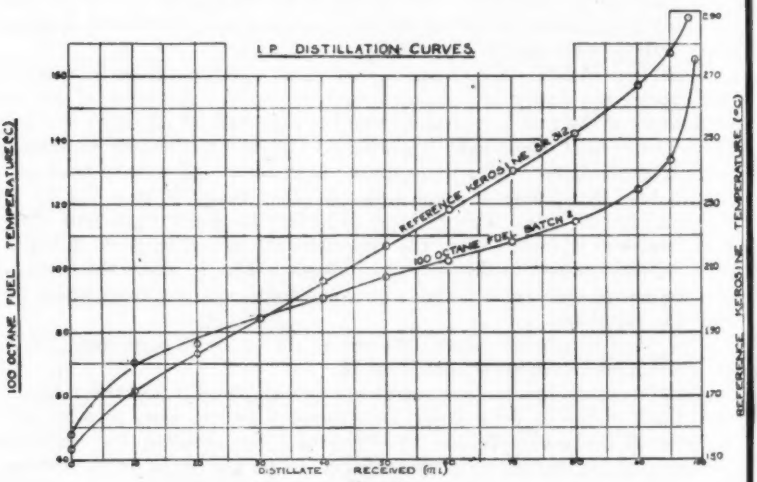

I.P. DISTILLATION CURVES
100 OCTANE FUEL TEMPERATURE (°C)
REFERENCE KEROSINE TEMPERATURE (°C)
REFERENCE KEROSINE BATCH 2
100 OCTANE FUEL BATCH 5
DISTILLATE RECEIVED (ml.)

FIG. 2.

A.S.T.M. DISTILLATION CURVES FOR 100 OCTANE FUEL AND KEROSINE.

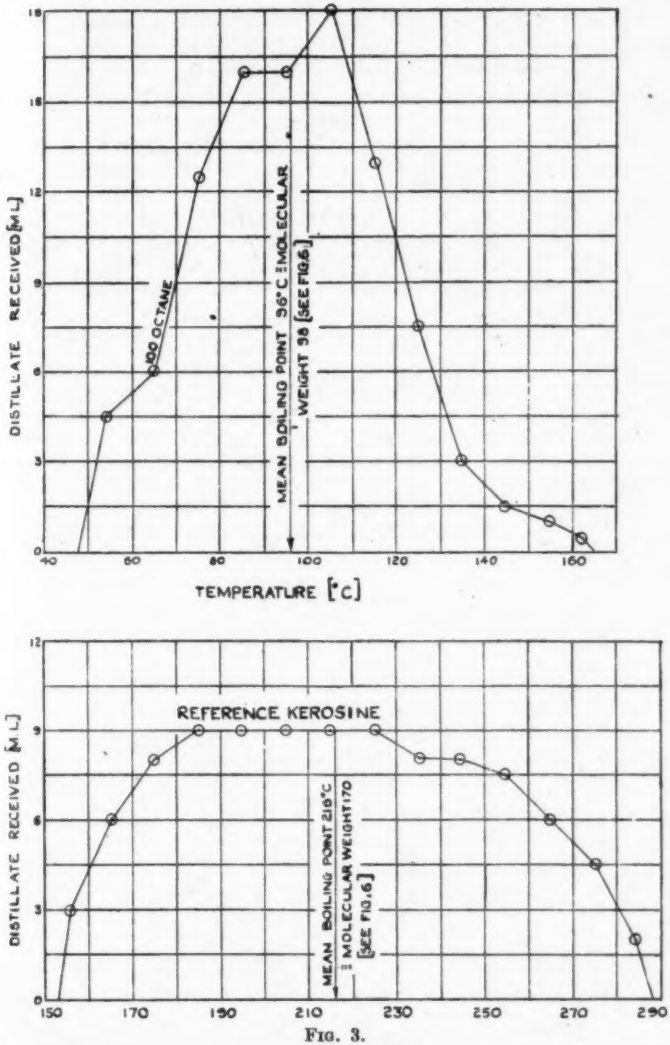


FIG. 3.

DIFFERENTIAL DISTILLATION CURVES FOR 100 OCTANE FUEL AND KEROSINE.

3. EXPERIMENTAL METHODS.

3.1. *Description of Methods.*

3.11. *Vapour-Pressures.* The vapour-pressure of hydrocarbon mixtures was measured directly by Wilson and Barnard,[1] Rhodes and McConnell,[20]

Lewis,[21] and Brown,[22] who paid insufficient attention to the minimizing of the vapour space and loss of volatile fractions by free venting.

Indirect methods of measuring vapour-pressures were employed by Tizard and Marshall,[23] by Cadman,[24] by Oberfell, Alden, and Hepp,[25] and by Brown.[22] The first two sets of investigators used essentially the same principle, which depended on the addition of varying amounts of liquid to a fixed volume. Allowances were made for the inaccuracies caused by air in the apparatus, dissolved gases, and changing composition of the fuel with vaporization. Oberfell, Alden, and Hepp employed two columns of vapour space, but theirs was a semi-commercial method, and did not yield precise measurements. The method of Brown which depended on the use of several vapour volumes at each temperature and on extrapolation to zero vapour space was the most accurate.

3.12. *Normal Dew-Points.* The equilibrium boiling-points of fuels were measured by Whatmough,[26, 27] and a description of his apparatus and results was published in 1926. The fuel was boiled under equilibrium conditions (*i.e.*, input equal to output) in a special boiler in which a mixture of constant quality was maintained automatically; accuracy of measurement was of the order of $\pm 4°$ C. Ormandy and Craven [28] used this method for British fuels.

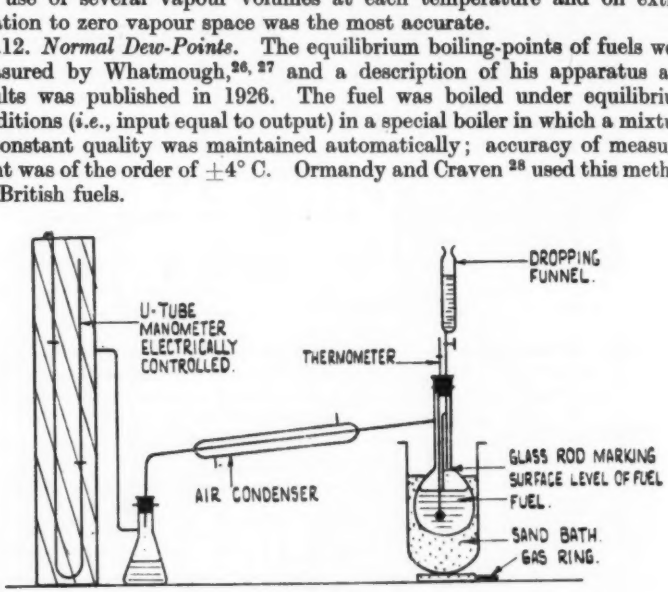


FIG. 4.

CONTINUOUS DISTILLATION APPARATUS.

The amounts of gasoline vaporized under conditions approaching equilibrium were determined by James,[29] and later Brown,[30] by passage of the fuel through a heated tube and spiral respectively at a pressure of one atmosphere; the curves obtained were extrapolated to 100 per cent vaporized to give the normal dew-points. Leslie and Good [31] also considered this problem.

Theoretically the normal dew-point of a gasoline is identical with Wilson and Barnard's atmospheric equilibrium solution temperature,[1] Stevenson and Stark's Deppé end-point,[15] Stevenson and Babor's equilibrium end-point,[11] and Whatnough's equilibrium boiling-point.[26, 27]

Podbielniak and Brown [32] have described and used an equilibrium

vaporization apparatus, whilst numerous instruments for the direct measurement of the dew-point of hydrocarbon vapours or gases have been devised for use in industry or the laboratory,[33-43] and some of these have been patented. Deaton and Frost [44] designed an apparatus for determining the dew-point of gases under pressure.

3.13. *Dew-Points of Air/Fuel Mixtures.* Gruse [12] passed various mixtures of air and fuel from 10 : 1 to 18 : 1 through a preheating coil and measured both the appearance and disappearance of dew on a metallic mirror cooled internally.

An equilibrium air-distillation apparatus was invented by Sligh,[45-47] who measured many dew-points of various air/fuel mixtures. Brown [16] used a slightly modified Sligh apparatus and measured a large number of 12 : 1 dew-points.

Stevenson and Babor,[11] employing a dynamic method and using a platinum-black surface, obtained the dew-points of seven gasolines for mixtures from 1 : 1 to 30 : 1. A modified form of Stevenson and Babor's apparatus was used by Bridgman [3] to determine the dew-point of air–gasoline mixtures ranging from 1 : 1 to 16 : 1.

3.2. *Experiments on Kerosine and Gas Oil.*

An equilibrium distillation apparatus (Fig. 4) was set up after the manner described by Wilson and Barnard [1] and 200-ml. fuel was distilled

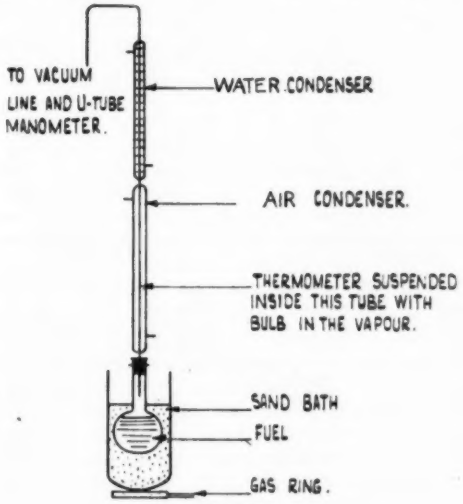


FIG. 5.

SPECIAL REFLUX APPARATUS.

continuously for 5½ hours, after which time approximately 10 times as much liquid had passed through the flask as was held there. A pressure of 117-mm mercury abs. was employed for the kerosine and a pressure of 29 mm mercury abs for the gas oil. In each case a constant temperature

was reached, and at this stage the fuel in the flask—*i.e.*, the equilibrium solution—was in a state of dynamic equilibrium, and the composition of the gases distilling over was the same as that of the fuel entering as liquid through the dropping funnel. The liquid in the flask was in equilibrium with this outgoing vapour, as its temperature remained steady, and therefore had the same composition as that of the liquid which would first condense out from this outgoing vapour at its dew-point.

A sample of each equilibrium solution thus prepared and a sample of the original kerosine and gas oil were used for the determination of the bubble-point/pressure and dew-point/pressure curves. This was accomplished by the reflux apparatus shown in Fig. 5 which could be maintained at a constant reduced pressure by means of an automatic pressure regulator consisting of a Schroder valve operated electrically by small oscillations of the mercury in a U-tube manometer.

3.3. *Results for Kerosine and Gas Oil.*

The experimental results are given in Table III.

TABLE III.

Experimental Results for Kerosine and Gas Oil.

Kerosine.		Gas Oil.	
Absolute pressure, mm Hg.	Reflux temperature, ° C.	Absolute pressure, mm Hg.	Reflux temperature, ° C.
122	142	74	115
302	165	200	150
462	177	402	174
612	189	553	186
762	196	760	200
Kerosine Equilibrium Solution.		Gas Oil Equilibrium Solution.	
Absolute pressure, mm Hg.	Reflux temperature, ° C.	Absolute pressure, mm Hg.	Reflux temperature, ° C.
125	194	65	185
305	226·5	198	226
465	239	400	250
605	247	541	262
765	255·5	760	276

Corrected for exposed stem.

Now the variation in the vapour pressure of a hydrocarbon mixture is given by the Clausius–Clapeyron relation :—

$$\frac{dP}{dt} = \frac{L}{(V - v)t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Neglecting the volume of the liquid, v, and rearranging, we have :—

$$dP = \frac{L}{V} \cdot \frac{dt}{t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Assuming the vapour to obey the gas law $PV = R^1t$ (14) becomes :—

$$\frac{dP}{P} = \frac{L}{R'} \cdot \frac{dt}{t^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Integrating (15) between two conditions 1 and 2, we have :—

$$\log_e P \Big|_1^2 = \frac{L}{R'} \cdot \left(-\frac{1}{t}\right)\Big|_1^2 \quad . \quad . \quad . \quad . \quad . \quad (16)$$

which indicates that if the vapour-pressure values of a given fuel (bubble-points) and the vapour-pressure values of a given equilibrium solution (dew-points) at various pressures be plotted on "log/reciprocal" graph paper, a straight line should result.

This has been done in Fig. 1, and straight lines were obtained; these were extrapolated to both higher and lower pressures.

4. Theoretical Methods.

4.1. *Description of Methods.*

Hachmuth [48] has shown that the vapour-pressure equation for two and three component mixtures, respectively, may be written

$$y_A = P_A \cdot (\pi - P_B)/\pi \cdot (P_A - P_B) \quad . \quad . \quad . \quad . \quad (17)$$

$$y_A = \frac{P_A}{\pi}\left[\frac{P_c(\pi - P_B) + x_c' \cdot \pi(P_B - P_c)}{P_c \cdot (P_A - P_B)}\right] \quad . \quad . \quad (18)$$

For each additional component the equation practically doubles in complexity, and becomes almost unmanageable for more than three components. Unfortunately a dew-point curve for a two-component mixture gives no hint as to the form a general equation should take; an empirical equation covering such a curve becomes very complex if an accuracy of ± 5 or 10° C is required.

Franklin [49] has recently devised a simple nomographic chart for solving vapour-equilibrium problems for binary systems, whilst Nord [50] has designed a nomogram for ternary systems, based on constant relative volatilities, which gives the boiling-point of any mixture of known composition, and thence the molecular composition of the vapour.

Kennedy [51] has formulated an expression containing three constants characteristic of the individual fuels for determining the dew-point at different total pressures and air–fuel ratios. The theory rests on the assumption that over the range of pressures in question the composition of the first observable portion of liquid condensing just below the dew-point remains sensibly constant. The equation is :—

$$t_D = K_1 \Big/ \left[\log_{10} P - \log_{10}\left(1 - \frac{M_f}{M_a} \cdot R\right) - K_2\right] \quad . \quad . \quad (19)$$

Oberfell, Alden, and Hepp,[25] and Brown [22] have computed hydrocarbon vapour pressures on the basis of fractional analysis, whilst Perry,[52] and

more recently Huntingdon,[53] give several worked examples of a vapour-pressure computation for a ternary hydrocarbon mixture. A general extension and development of this method and an application to complex liquid hydrocarbon mixtures are given in the subsequent paragraph.

4.2. *Development of the "Integration Method."*

4.21. *Normal Bubble-Points and Dew-Points.* Now, by Dalton's Law we have :—

$$p_i = \pi \cdot V_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

and by Avogadro's hypothesis this becomes :—

$$p_i = \pi y_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Furthermore, Raoults' law may be written :—

$$p_i = P_i \cdot x_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

and by combining equations (21) and (22), we have :—

$$p_i = \pi y_i = P_i \cdot x_i (i = 1 \ldots n) \quad . \quad . \quad . \quad . \quad (23)$$

which expresses the relation between the pressures and molecular concentrations for a fuel in a state of liquid–vapour equilibrium.

Now, at the bubble point, t_B, we have by Definition 1 :—

$$x_i = x_{i_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

and

$$\sum_{i=1}^{n} P_i = \pi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Whilst at the dew-point, t_D, we have by Definition 2 :—

$$y_i = x_{i'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

The above results may now be applied to the study of the equilibrium of a mixture of n hydrocarbons—*i.e.*, a fuel, which, it will be assumed, behaves ideally.

Let us assume that component i is more volatile than component $(i + 1)$, for all i ranging from 1 to $(n - 1)$.

Under equilibrium conditions we shall have :—

$$\pi \cdot y_i = P_i x_i \, (i = 1, 2 \ldots n) \quad . \quad . \quad . \quad . \quad (27)$$

and

$$\sum_{1}^{n} \pi \cdot y_i = \sum_{1}^{n} P_i x_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

The question now arises how to employ equation (28) to calculate bubble-points and dew-points for a given fuel whose x_{i_0} are known, and whose P_i are known at different temperatures.

Remembering that by hypothesis

$$\sum_{1}^{n} x_q = 1 \, . \, (q = i, i_0 \text{ or } i') \quad . \quad . \quad . \quad . \quad (29)$$

Equation (28) may be simplified in two ways by using equation (27), giving :—

$$\pi = \sum_1^n P_i \,.\, x_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

and

$$1 = \sum_1^n \frac{\pi y}{P_i} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

Now, at the bubble-point the *individual* values of the x_i relating to the infinitesimal quantity of vapour above the liquid are unknown, and hence equation (31) is valueless, and equation (30) is the one to use, the values x_i being equal to the values x_{i_b} (by equation 24), which are known, *i.e.* :—

$$\pi = \sum_1^n P_i \,.\, x_{i_b} \text{ at } t_B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30a)$$

On the other hand, at the dew-point the *individual* values of the x_i relating to the infinitesimal quantity of liquid present are unknown, and equation (30) is valueless, and equation (31) is the one to use, the values y_i being equal to the values x_{i_d} (by equation 26) which are known—*i.e.* :—

$$1 = \sum_1^n \frac{\pi \,.\, x_{i_d}}{P_i} \text{ at } t_D \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31a)$$

Equation (30*a*) gives emphasis to the lighter components with the larger P values, whilst equation (31*a*) gives emphasis to the heavier components with the smaller P values.

4.22. *Bubble-Points and Dew-Points of Different Air/Fuel Mixtures.* The bubble-point or dew-point of an air/fuel mixture at any given total pressure is the same as that of the bubble-point or dew-point of the fuel alone at a pressure equal to the partial pressure of the fuel in the mixture.

The first stage, therefore, is to determine the partial pressure of the fuel, p_f, in any given air/fuel mixture, and this will depend on the molecular weight of the fuel and the mixture ratio.

According to Dalton's law of partial pressures we have :—

$$\pi = p_f + p_a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

or

$$\pi = p_f (1 + p_a/p_f) \quad . \quad . \quad . \quad . \quad . \quad . \quad (32a)$$

Similarly the partial pressures of the fuel and air are the sums of the partial pressures of their n and n^1 constituents respectively.

$$P_f = \frac{R'T}{V} \sum_1^n \frac{m_i}{M_i} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

$$P_a = \frac{R'T}{V} \sum_1^{n^1} \frac{m_i}{M_i} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

Lemma

$$\sum_1^n m_i \Big/ \frac{1}{n} \,.\, \sum_1^n M_i \doteqdot \sum_1^n \frac{m_i}{M_i} \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

when

$$m_i - m_j \ll M_i, \text{ for all } i, j.$$

and

$$m_i \ll \sum_1^n m_i, \text{ for all } i.$$

In the case where $m_i = 1/n$ (for all i) and the M_i increase in arithmetic progression from M_1 to M_n it may be shown that the error in equation (35) takes the form :—

$$E < \left[\frac{(Mn - M_1)}{2M_n \cdot M_1 \cdot n^2} \sum_{K=1}^{n/2} (n - 2K + 1)(M_{n-K+1} - M_K)\right] \times 100\% \quad . \quad (36)$$

These assumptions apply approximately to such fuels as are dealt with in this paper, and in the case of 100-octane fuel and kerosine, inequality (36) indicates an error of less than 3 per cent, which is of the same order of accuracy as the estimate of the mean molecular weights of the fuels.

We may therefore write :—

$$m_f/\overline{M}_f = \sum_1^n \frac{m_i}{M_i} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

If we adopt the value 29 for the mean molecular weight of air, M_a, we may also write :—

$$m_a/\overline{M}_a = \sum_1^{n'} \frac{m_i}{M_i} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

From equations (33), (34), (37), and (38) we have :—

$$p_a/p_f = \frac{m_a}{\overline{M}_a} \frac{\overline{M}_f}{m_f} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

Substituting equation (39) into equation (32a) we obtain :—

$$\pi = p_f\left(1 + \frac{\overline{M}_f}{\overline{M}_a} \cdot \frac{m_a}{m_f}\right) . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

Calling $m_a/m_f = R$, the air/fuel ratio and rearranging equation (40) we obtain finally,

$$p_f = \pi\left(\frac{29}{29 + R.\,\overline{M}_f}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

The final stage in estimating the bubble-point or dew-point of an air/fuel mixture is to read off, from the appropriate bubble-point or dew-point curve in Fig. 1, the temperature corresponding to the fuel's partial pressure (calculated from equation 41). This temperature is the required bubble-point or dew-point.

4.23. *The "Integration Method."* The x_{i_0} are deduced from the true boiling-point distillation curve for the fuel by a method of tabulation; this involves the splitting up of the distillation curve into small "cuts" (or fractions) of 5–10° C range ($n = 10$ to 20), and the use of empirical charts for hydrocarbon liquids of mid-boiling-point plotted against mean molecular weight, and against specific gravity (alternatively, the specific gravity of the various fractions distilling may be measured). A small correction to the molecular weight/mid-boiling-point curve may have to be made in certain parts to allow for the presence of any high-density, low-molecular-weight aromatic hydrocarbons (see Fig. 6).

The P_i are deduced from empirical charts for hydrocarbons with mid-boiling-point plotted against temperatures and vapour-pressures (see Fig. 7).

Calculation of Bubble-Points. A guess t_1 is made of the normal bubble-point, and the corresponding $P_i^{t_1}$ are deduced from the vapour-pressure chart (Fig. 7). The sum on the right-hand side of the equation (30a) is

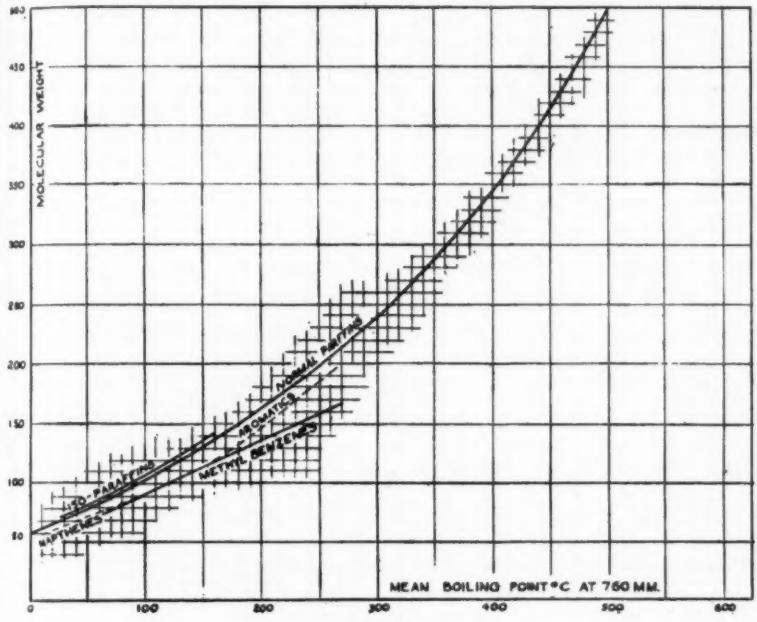


FIG. 6.

MOLECULAR WEIGHT *v.* HYDROCARBON BOILING POINT.

formed, and will be equal to π, if $t_1 = t_{NB}$; this sum will be $>$ or $<$, according as t_1 is $>$ or $< t_{NB}$.

If, as usually will be the case, $t_1 \neq t_{NB}$, then a new temperature t_2 must be chosen, and the new sum $\sum_1^n P_i^{t_2} x_{i_0}$ must be formed; this procedure must be repeated * until the sum equals π (to within 1 or 2 per cent).

* A method for converging rapidly to t_{NB} suggested itself during an extension of the theory under para. 4.21 above, to the case of a fuel possessing an infinity of components. The method is as follows:—

If for t_1 the sum equals πt_1 ($\neq \pi$), then we consider the hydrocarbon which boils at temperature t_1 under pressure πt_1, and find a new temperature t_2, at which this hydrocarbon will boil under a pressure π, by reference to Fig. 7. If $(t_1 \sim t_{NB}) < 20°$ C, we shall find that t_2 lies within 2 or 3° C of the true value of t_{NB}. Temperature t_{NB} may be obtained by forming the sum $\sum_1^n P_i^{t_2} x_{i_0}$ and once again referring to Fig. 7.

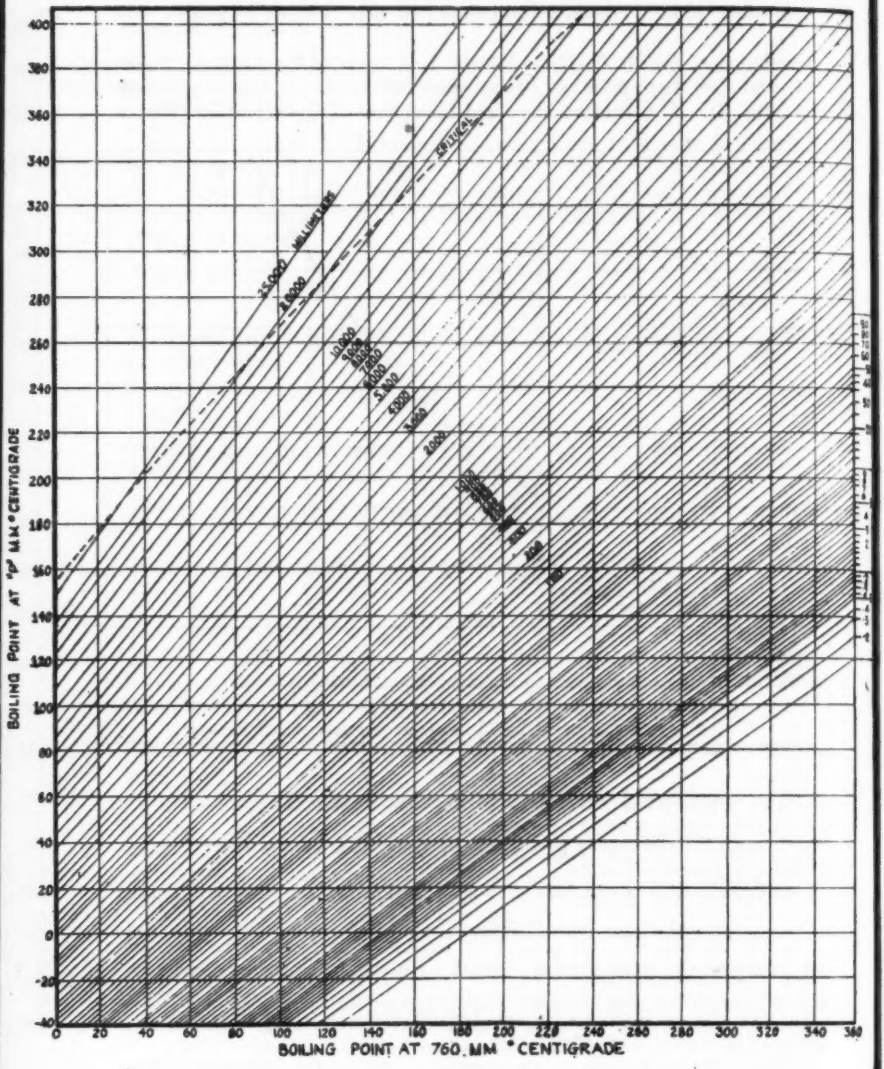


FIG. 7.

BOILING POINT AT P MM HG v. HYDROCARBON BOILING POINT.

Bubble-points of air/fuel mixtures may be calculated from the normal bubble-point curves (see Fig. 1) by the method outlined in para. 4.22 above.

Calculation of Dew-Points. Our working equation is equation (31a); the x_i, and P_i are calculated as described above, and the sum on the right-hand side of this equation is formed for values of P_i at some guessed normal dew-point temperature t_1. The sum will be $>$ or <1, according as t_1 is $<$ or $> t_{ND}$.

If, as usually will be the case, $t_1 \neq t_{ND}$, then other temperatures, t_2, t_3, etc., must be chosen until the sum equals unity (to within 1 or 2 per cent). The rapid method for converging to t_{NB} may be applied to the case of the dew-point if first we multiply our sum by π.

Dew-points of air/fuel mixtures may be calculated from the normal dew-point curves (see Fig. 1) by the method outlined in para. 4.22 above.

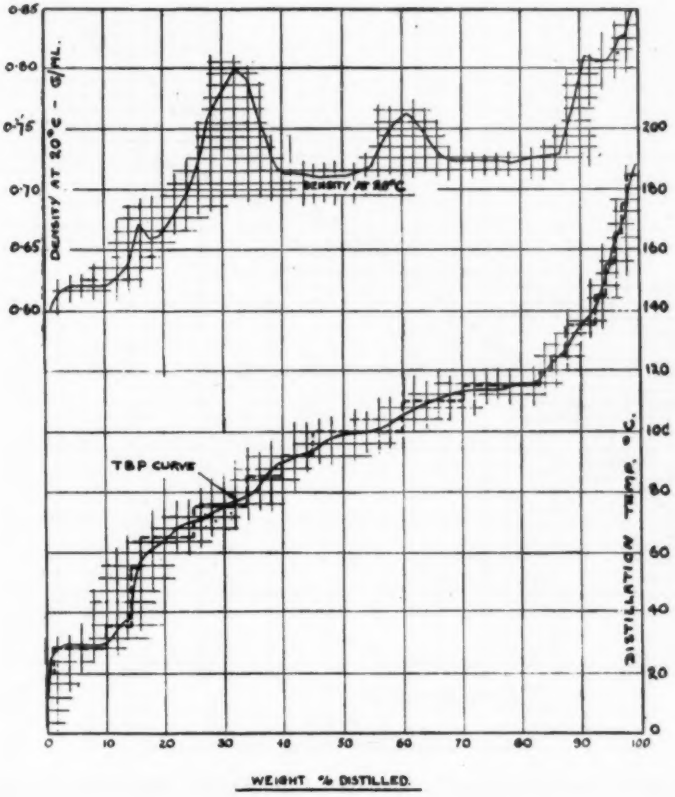


FIG. 8.

T.B.P. DISTILLATION CURVE FOR 100 OCTANE FUEL.

4.3. *Results for 100-Octane Fuel and Kerosine.*

Samples of reference kerosine SR 312 and 100-octane fuel batch 2 were distilled by the Anglo-Iranian Oil Co. The 100-octane fuel was distilled in a 40-plate atmospheric column, whilst the kerosine was distilled in a

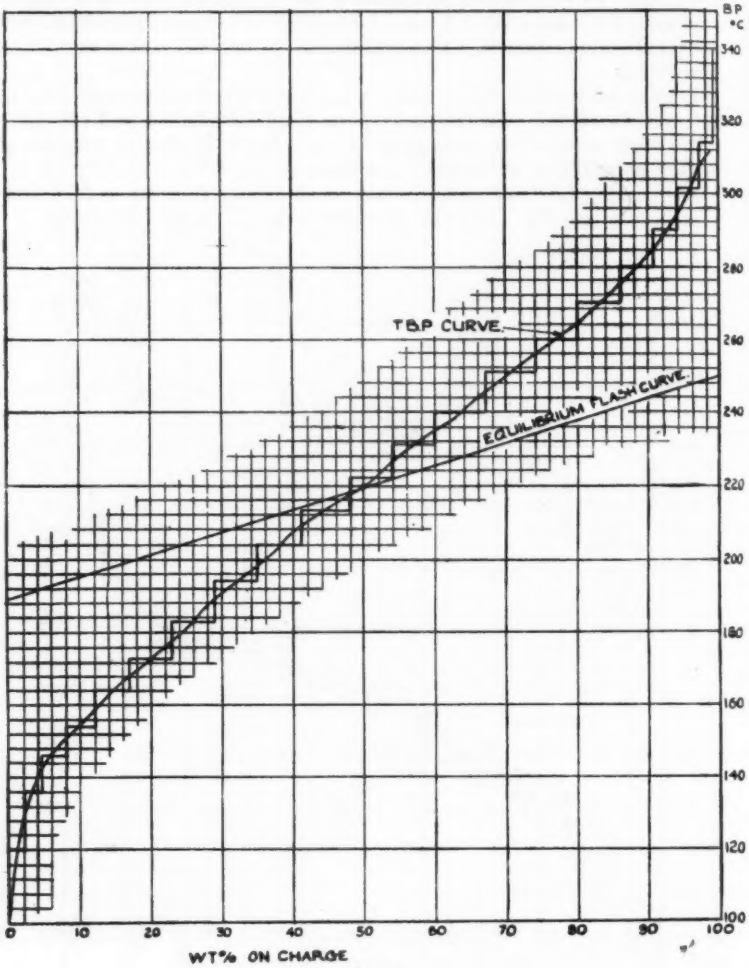


FIG. 9.

T.B.P. DISTILLATION CURVE FOR KEROSINE.

14-plate vacuum column. The true boiling-point distillation curves so obtained are reproduced in Figs. 8 and 9, and the computations from these true boiling-point curves are shown in Tables IV and V.

TABLE IV.

100-Octane Fuel, Batch 2.

Calculations from T.B.P. Curve.

Component *i*.	Boiling range, °C.	Mean boiling-point, °C.	Wt.-%.	Mol. wt.	Mols.	$100x_i$.
1	3–27	20	0·5	58	0·0086	0·82
2	27–29	28·5	9·5	72	0·1319	12·71
3	29–45	35	4·5	72	0·0625	6·02
4	45–58	55	1·5	78	0·0192	1·85
5	58–70	65	9·0	86	0·1046	10·08
6	70–78	75	9·0	88	0·1023	9·86
7	78–90	85	6·0	90	0·0667	6·43
8	90–94	92	5·0	100	0·0500	4·82
9	94–105	100	15·0	114	0·1316	12·68
10	105–113	110	10·0	100	0·1000	9·64
11	113–118	115	13·0	114	0·1140	10·98
12	118–123	120	2·0	110	0·0182	1·75
13	123–127	125	2·5	110	0·0227	2·19
14	127–140	135	5·0	110	0·0454	4·37
15	140–151	145	2·0	117	0·0171	1·65
16	151–158	155	1·0	124	0·0081	0·78
17	158–168	165	1·5	124	0·0121	1·17
18	168–179	175	1·0	124	0·0081	0·78
19	179–190	185	2·0	138	0·0145	1·39
			100·0		1·0376	99·97

TABLE V.

Reference Kerosine, SR. 312.

Calculations from T.B.P. Curve.

Component *i*.	Boiling range, °C.	Mid-boiling point, °C.	Wt.-%.	Mol. wt.	Mols.	$100x_i$.
1	100–130	115	2·0	100	0·02000	3·18
2	130–141	135·5	2·5	113	0·02210	3·51
3	141–150	145·5	3·5	116	0·03017	4·79
4	150–159	154·5	4·0	121	0·03306	5·25
5	159–168	163·5	5·0	126	0·03968	6·31
6	168–178	173	6·0	132	0·04545	7·22
7	178–189	183·5	6·0	138	0·04347	6·91
8	189–198	193·5	6·0	145	0·04138	6·58
9	198–209	203·5	6·0	152	0·03947	6·27
10	209–217	213	7·0	159	0·04403	7·00
11	217–227	222	6·0	165	0·03636	5·78
12	227–235	231	6·0	171	0·03509	5·58
13	235–246	240·5	7·0	179	0·03911	6·21
14	246–256	251	7·0	187	0·03743	5·95
15	256–265	260·5	6·0	195	0·03077	4·89
16	265–275	270	6·0	204	0·02941	4·67
17	275–285	280	4·5	211	0·02133	3·39
18	285–295	290	3·5	220	0·01591	2·53
19	295–307	301	3·0	230	0·01304	2·07
20	307–325	316	2·0	245	0·00816	1·30
21	325–340	332·5	1·0	260	0·00385	0·61
			100·0		0·62927	100·00

Worked examples of a normal bubble-point and a normal dew-point calculation are given in Tables VI and VII. Results of normal bubble-

TABLE VI.

Method for Computing Bubble-Point.

Reference Kerosine at 760 mm Pressure.

Component No.	$100x_{i_0}$.	First attempt (170° C).		Second attempt (186° C).	
		P_i^{170} (mm).	$\Sigma P_i^{170} x_{i_0}$.	P_i^{186} (mm).	$\Sigma P_i^{186} x_{i_0}$.
1	3·18	2450	77·9	4000	127·2
2	3·51	1800	63·1	2600	91·2
3	4·79	1410	67·5	2000	95·8
4	5·25	1110	58·2	1650	86·5
5	6·31	900	56·8	1320	83·3
6	7·22	700	50·5	1010	72·8
7	6·91	545	37·7	810	56·0
8	6·58	410	27·0	635	41·8
9	6·27	308	19·3	497	31·2
10	7·00	240	16·8	380	26·6
11	5·78	183	10·6	298	17·2
12	5·58	140	7·8	235	13·1
13	6·21	108	6·7	180	11·2
14	5·95	80	4·8	135	8·0
15	4·89	60	3·0	100	4·9
16	4·67	44	2·1	78	3·6
17	3·39	32	1·1	59	2·0
18	2·53	23·5	0·6	42	1·1
19	2·07	16·5	0·3	30	0·6
20	1·30	9·5	0·1	19	0·2
21	0·61	5·0	—	11	0·1
Totals :	100·0		511·9		774·4

See para. 4.23.

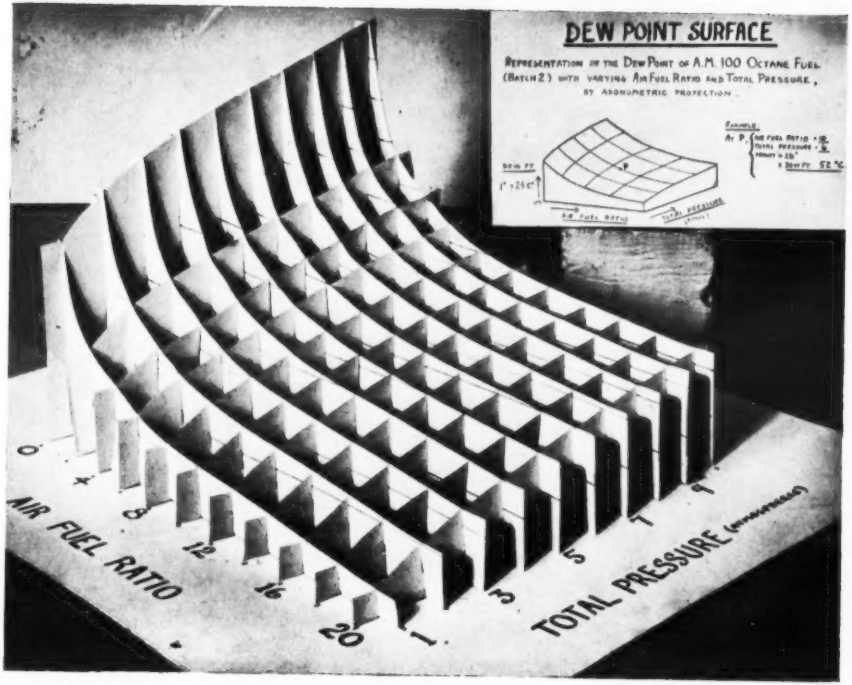
$t_1 = 170°$ C and $\pi t_1 < 760$; $\therefore t_1 < t_B$.
By Fig. 7, $t_2^1 = 186°$ C, but $\pi t_2^1 \doteq 760$.
Hence required boiling-point is 186° C.

point and normal dew-point estimations for both 100-octane fuel and kerosine over a range of pressures are set out in Table VIII.

The valuable assistance rendered by the Anglo-Iranian Oil Co.[54] in this work, particularly for the normal dew-points at super-atmospheric pressures which were estimated by them, is gratefully acknowledged. The equilibrium flash-curves for the two fuels were determined by them by the method of Piroomov and Beiswinger,[55, 56] and used to obtain the first approximation to the normal dew-points.

The normal bubble-point and dew-point values have been plotted in Fig. 1 ; it will be seen that, up to a pressure of 3 atmospheres, straight lines were obtained. The probable error in these values is ± 2 to 5° C.

These curves for 100-octane fuel and kerosine, and also the curves obtained experimentally for gas-oil (Fig. 1), were used (extrapolated to



[To face p. 735.

FIG. 19.

DEW-POINT SURFACE FOR 100-OCTANE FUEL.

TABLE VII.

Method for Computing Dew-point.

100-Octane Fuel at 100 mm Pressure.

Component no.	$100x_i$.	First attempt (50° C).		Second attempt (58° C).		Third attempt (56° C).	
		$\left(P_i^{50}\frac{100}{\pi}\right)$.*	$\Sigma\frac{\pi x_i}{P_i}$.	$\left(P_i^{58}\frac{100}{\pi}\right)$.	$\Sigma\frac{\pi x_i}{P_i}$.	$\left(P_i^{56}\frac{100}{\pi}\right)$.	$\Sigma\frac{\pi x_i}{P_i}$.
1	0·82	2000	0·0005	2500	0·0003	2350	0·0003
2	12·71	1550	0·0082	1940	0·0065	1815	0·0070
3	6·02	1220	0·0049	1600	0·0038	1410	0·0043
4	1·85	650	0·0028	855	0·0022	800	0·0232
5	10·08	470	0·0214	615	0·0164	580	0·0174
6	9·86	330	0·0299	445	0·0222	420	0·0235
7	6·43	240	0·0268	320	0·0201	297	0·0216
8	4·82	180	0·0268	254	0·0190	235	0·0205
9	12·68	135	0·0938	188	0·0673	174	0·0728
10	9·64	95	0·1015	130	0·0740	120	0·0803
11	10·98	80	0·1371	110	0·0997	100	0·1098
12	1·75	65	0·0269	91	0·0175	84	0·0208
13	2·19	52·5	0·0417	77·5	0·0283	70	0·0313
14	4·37	35	0·1250	51	0·0857	46	0·0951
15	1·65	24	0·0688	34·5	0·0478	31	0·0532
16	0·78	16	0·0487	24	0·0325	21	0·0372
17	1·17	10	0·1170	16	0·0732	14	0·0835
18	0·78	6·4	0·1220	10	0·0780	9	0·0867
19	1·39	3·95	0·3520	6·5	0·2139	5·8	0·2398
Totals :	99·97		1·3558		0·9084		1·0283

* $= P_{i_0}^{50}$ in this case.

See para. 4.23.

$t_1 = 50°$ C and (π the sum) > 760; $\therefore t_1 < t_D$.
By Fig. 7, $t_2^1 = 58°$ C, but (π the sum) < 760; $\therefore t_2^1 > t_D$.
By Fig. 7 $t_3^1 = 56°$ C, now (π the sum) $\div 760$.
Hence required dew-point is 56° C.

low pressures) as the bases of the calculation of bubble-points and dew-points for air/fuel mixtures (1 : 1 to 20 : 1).

An approximate method of determining the mean molecular weight of a fuel is shown in Fig. 3; other methods, such as forming the sum $\sum_1^n M_i x_i$ (from Tables IV and V) and the empirical methods of Watson and Nelson,[57–60] were also used. Values 98, 165, and 188 were adopted for 100-octane fuel, kerosine, and gas oil, respectively.

The bubble-point and dew-point results for air/fuel mixtures (0 : 1 to 20 : 1) over various pressure ranges are presented as a set of nine nomograms [61, 62] (Figs. 10–18).

Finally, the variation in the dew-point of 100-octane fuel with total pressure and air/fuel ratio was depicted by a surface in three dimensions (Fig. 19).

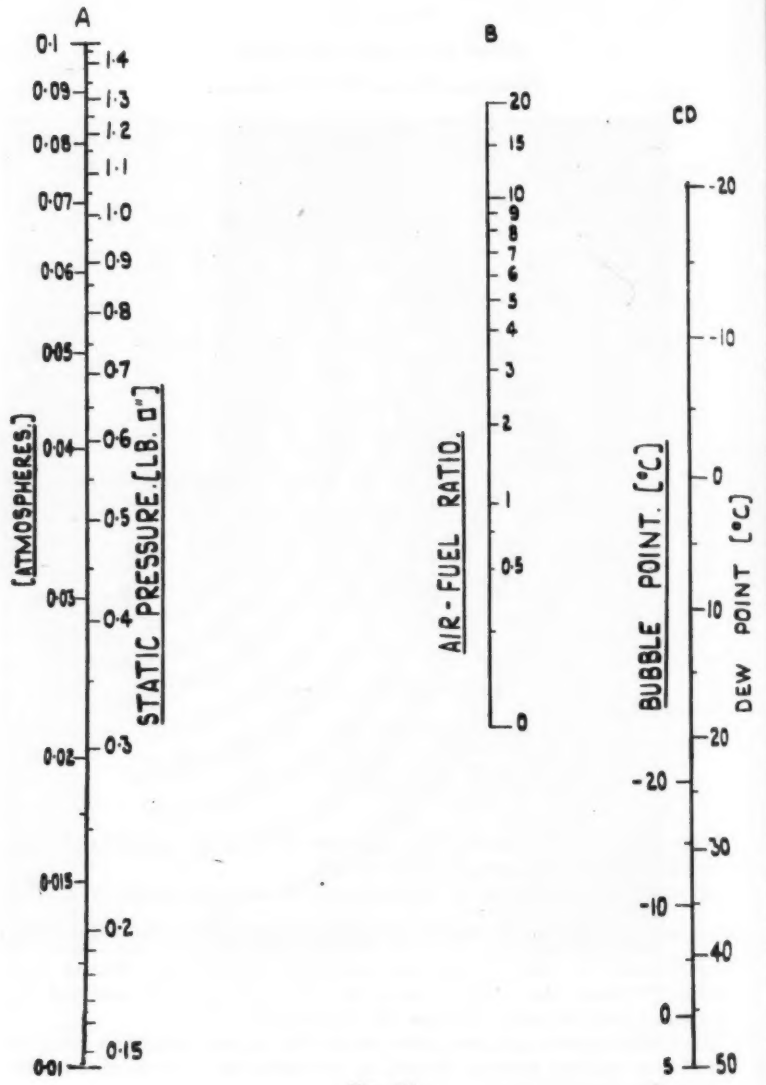


FIG. 10.

BUBBLE-POINT AND DEW-POINT NOMOGRAM FOR 100-OCTANE FUEL AT VERY LOW PRESSURES.

Note.—Scales A, B, C and A, B, D are used in conjunction.

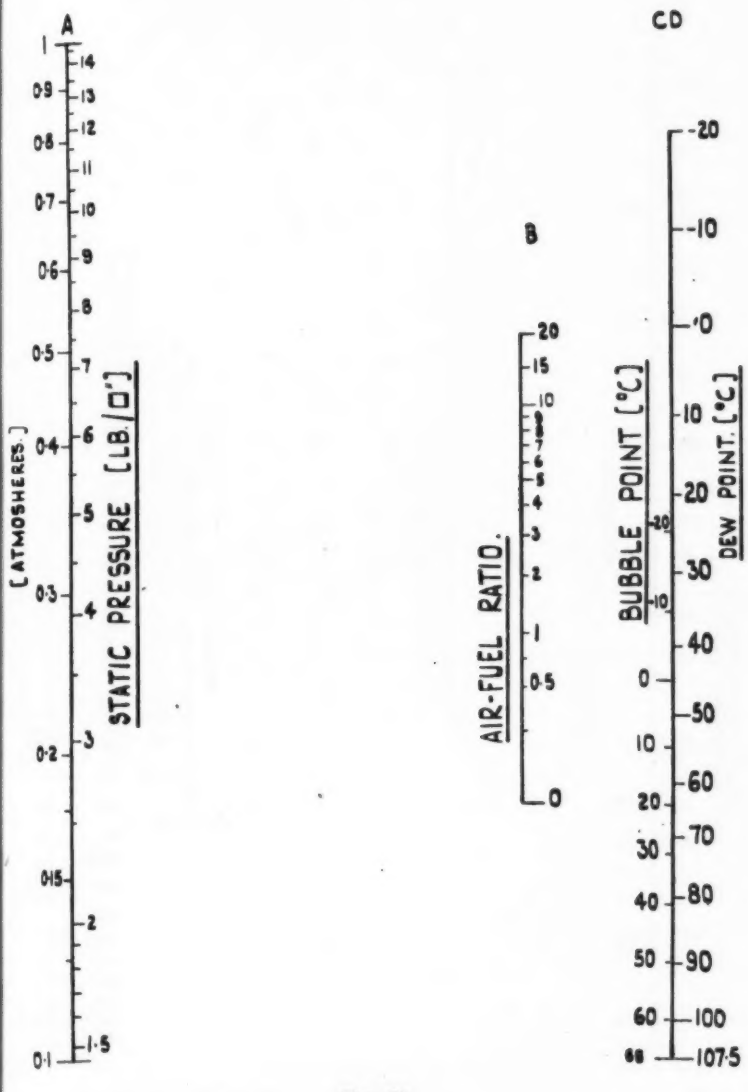


FIG. 11.

BUBBLE-POINT AND DEW-POINT NOMOGRAM FOR 100-OCTANE FUEL AT LOW PRESSURES.

Note.—Scales A, B, C and A, B, D are used in conjunction.

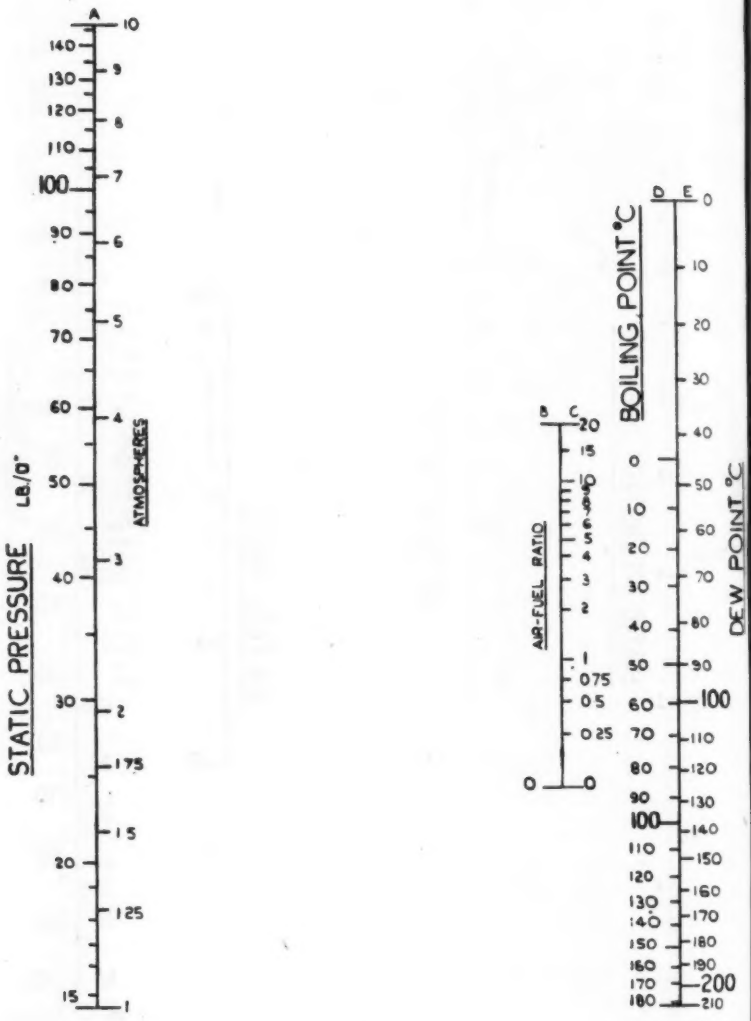


FIG. 12.

BUBBLE-POINT AND DEW-POINT NOMOGRAM FOR 100-OCTANE FUEL AT HIGH PRESSURES

Note.—Scales A, B, D and A, C, E are used in conjunction.

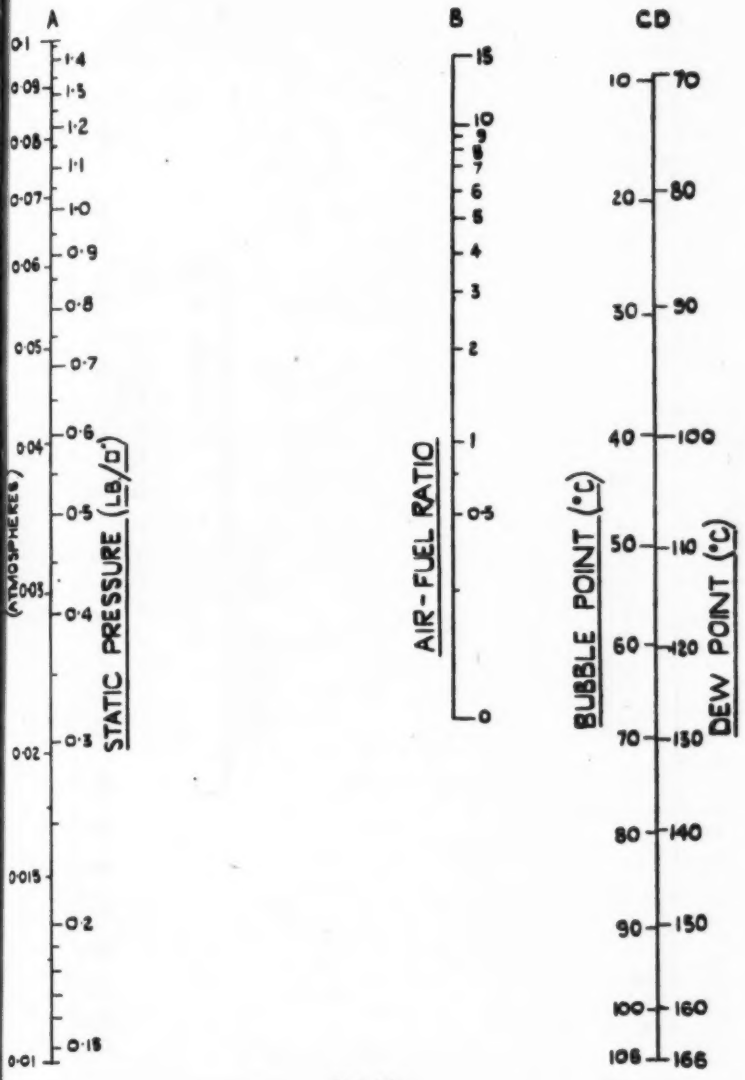


FIG. 13.

BUBBLE-POINT AND DEW-POINT NOMOGRAM FOR KEROSINE AT VERY LOW PRESSURES.

Note.—Scales A, B, C and A, B, D are used in conjunction.

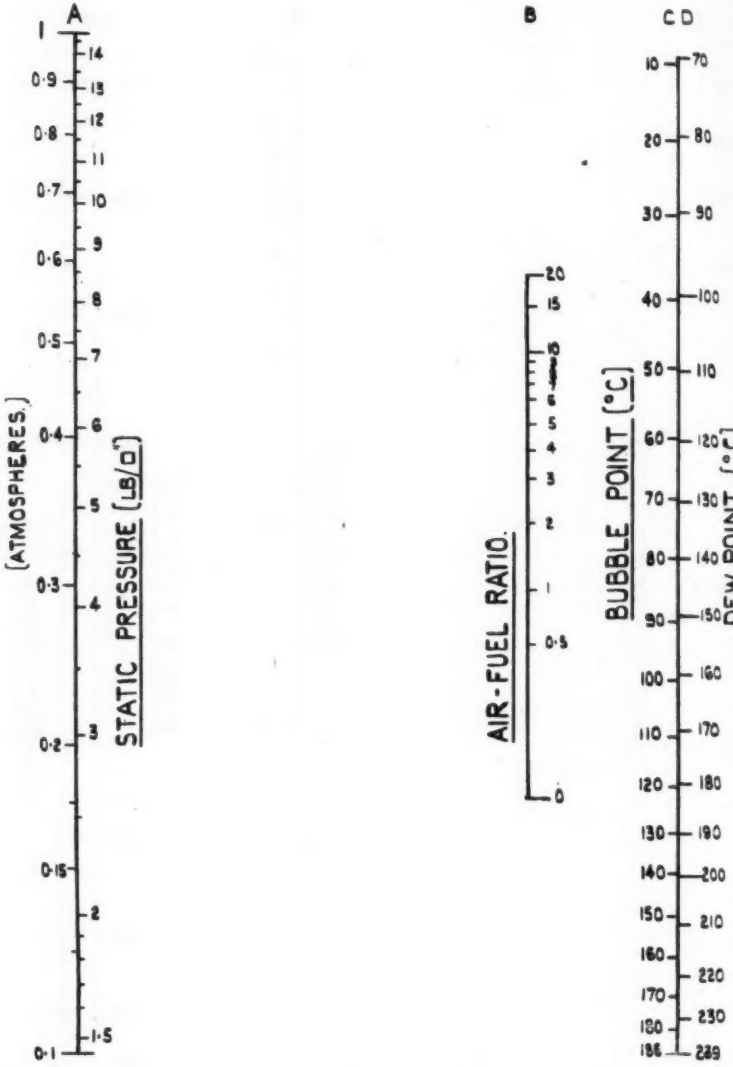


FIG. 14.

BUBBLE-POINT AND DEW-POINT NOMOGRAM FOR KEROSINE AT LOW PRESSURES.

Note.—Scales A, B, C and A, B, D are used in conjunction.

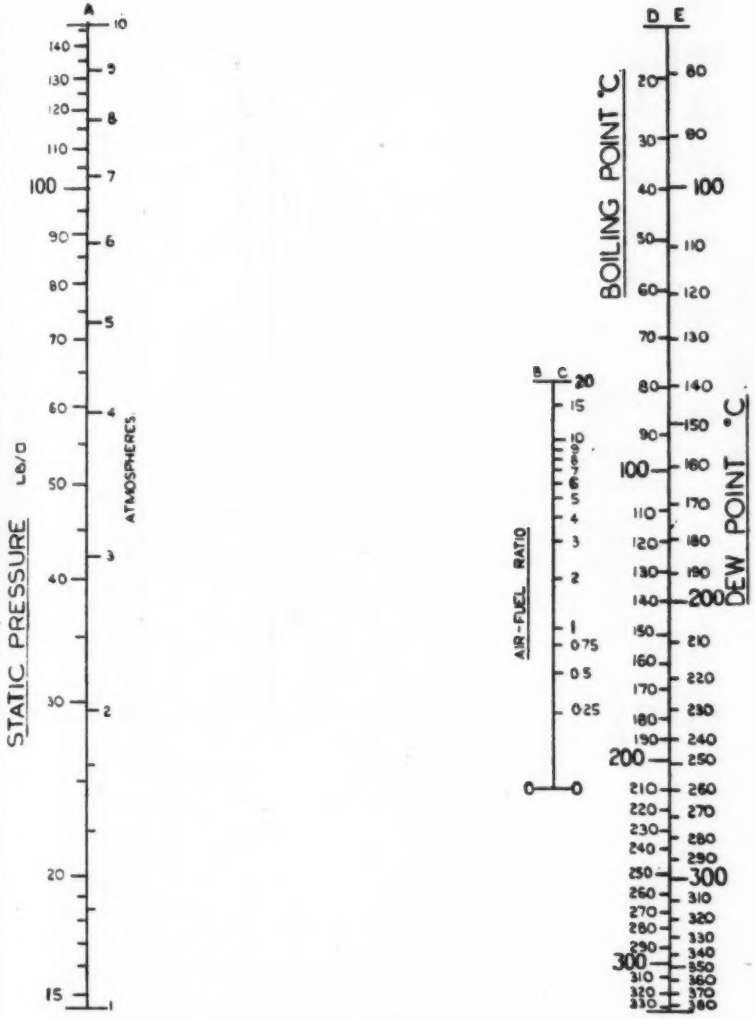


FIG. 15.

BOILING-POINT AND DEW-POINT NOMOGRAM FOR KEROSINE AT HIGH PRESSURES.

Note.—Scales A, B, D and A. C, E are used in conjunction.

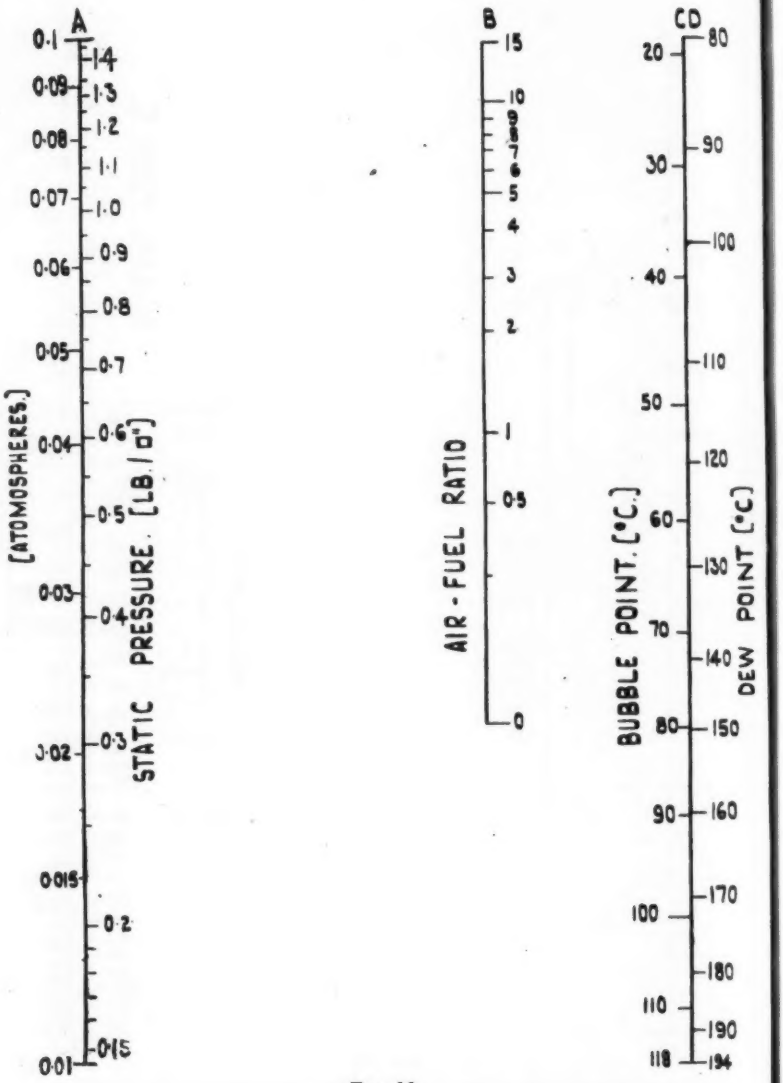


FIG. 16.

BUBBLE-POINT AND DEW-POINT NOMOGRAM FOR GAS OIL AT VERY LOW PRESSURES.

Note.—Scales A, B, C and A, B, D are used in conjunction.

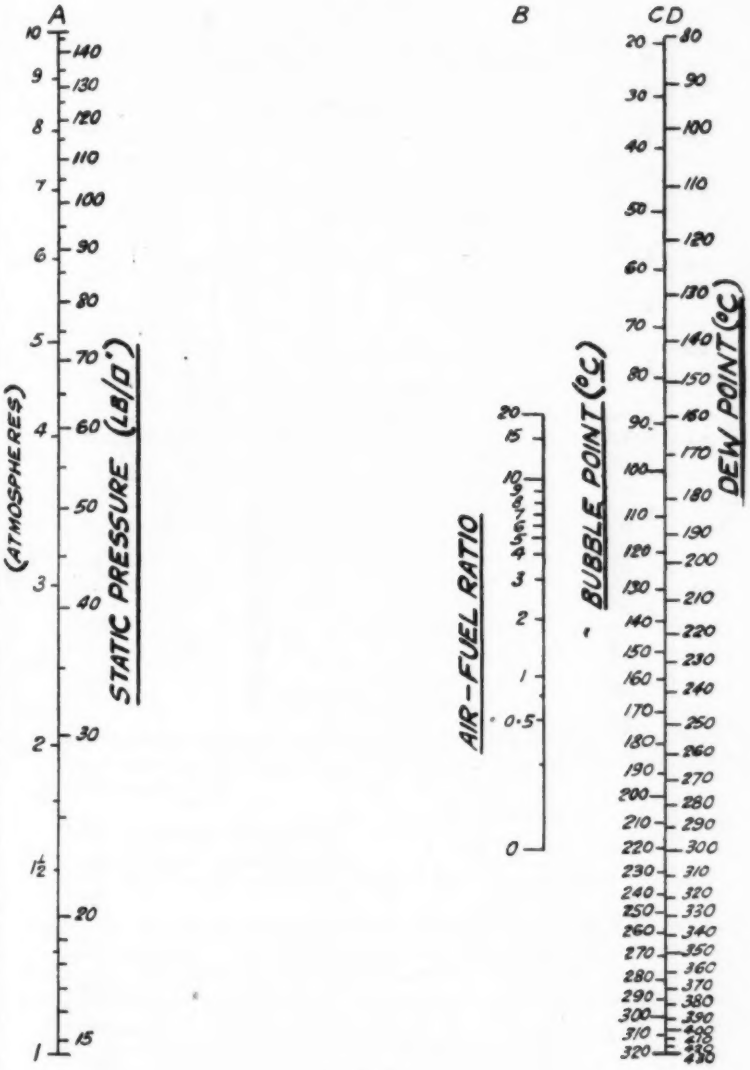


FIG. 17.

BUBBLE-POINT AND DEW-POINT NOMOGRAM FOR GAS OIL AT LOW PRESSURES.

Note.—Scales A, B, C and A, B, D are used in conjunction.

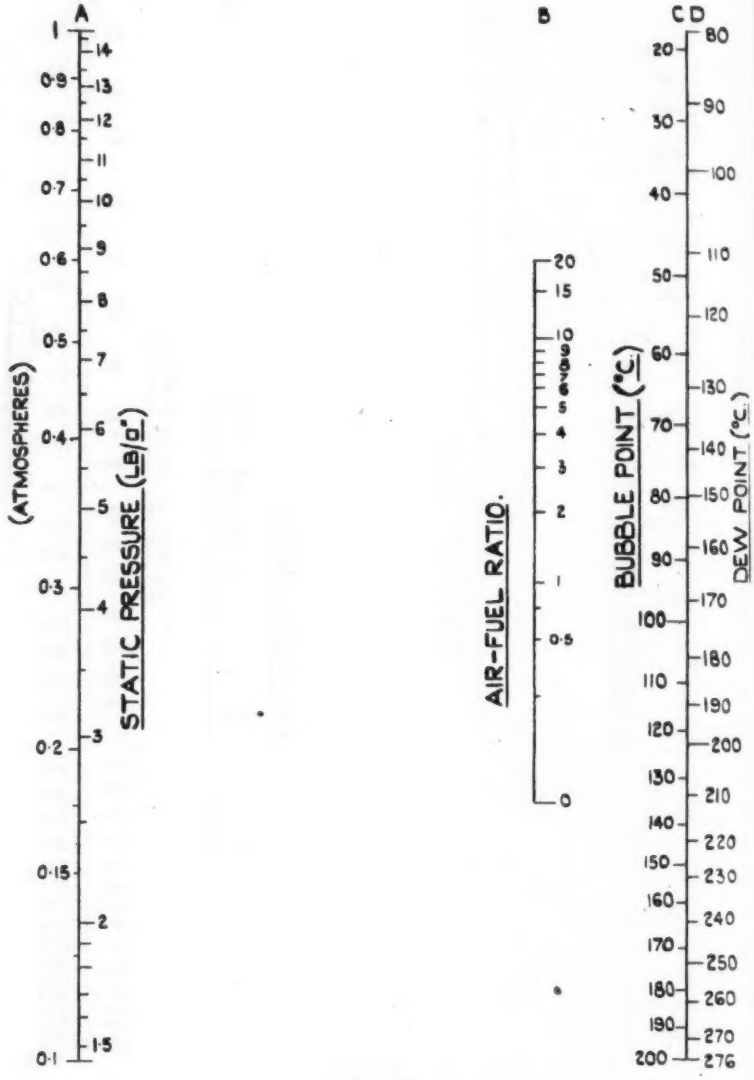


FIG. 18.

BUBBLE-POINT AND DEW-POINT NOMOGRAM FOR GAS OIL AT HIGH PRESSURES.

Note.—Scales A, B, C and A, B, D are used in conjunction.

TABLE VIII.

Normal Bubble-Point and Normal Dew-Point Values for 100-Octane Fuel, Kerosine and Gas Oil at Various Pressures.

Normal Bubble-points (° C).

Pressure, mm Hg.	100-Octane.	Kerosine.	Gas oil.
50	−4	94	107
100	11	112·5	126
300	40	150	163
500	56	170	184
760	68	186	200
2100	106	237	249
5150	145	286	298
7700	165	312	322

Normal Dew-points (° C).

Pressure, mm Hg.	100-Octane.	Kerosine.	Gas oil.
50	41·5	155	180
100	56	173	202
300	82	208	239
500	96	225	260
760	107·5	239	276
2100	144	283	328
5150	185	335	390
7700	208	363	430

5. GENERAL CONCLUSIONS.

There are three general methods of determining the boiling-points of a liquid hydrocarbon fuel under various conditions of air dilution and total pressure, namely :—

(*a*) Empirical estimation;
(*b*) Practical measurement;
(*c*) Theoretical calculation from T.B.P. distillation curve.

Of these, the empirical method is the most convenient, and the practical the most accurate. The latter necessitates the most exacting control of conditions, and involves considerable practical elaboration and refinement, whilst the former, though simple, requiring no practical information other than a standard A.S.T.M. distillation of the fuel, gives very unreliable results, particularly for fuels outside the gasoline range.

The theoretical method is the ideal compromise, since it yields reliable results and requires only the determination of the fuel's true boiling-point distillation curve, an experiment which is carried out as a routine test in the petroleum industry. This method has been fully developed and explained in this paper, and has been applied to the two fuels—100-octane and kerosine.

Consequently, given only this paper and the true boiling-point curve of a liquid hydrocarbon fuel, it would be possible to estimate the bubble-points and dew-points of that fuel within the total pressure range 1/100 to 10 atmospheres, and between air/fuel limits of, say, 0 : 1 to 20 : 1, with an accuracy of $\pm 10°$ C, or $\pm 5°$ C if the fuel were mainly paraffinic.

Acknowledgment.

Figs. 8 and 9 and Tables IV and V are due to the Anglo-Iranian Oil Co., and the generous assistance given by this organization in connection with the calculation of normal dew-points is gratefully acknowledged.

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OBITUARY.

FREDERICK EDWARD CHERRY.

It is with regret that we record the death on November 18, 1946, of Frederick Edward Cherry, who became a Member of the Institute in 1920, and a Fellow in 1939.

Born in 1888 he first entered the petroleum industry in 1909, when he was employed in Russia with the Maikop Standard Oilfields Ltd. He subsequently joined the Scottish Maikop Oilfields Ltd., the Russian Rotory Boring Co. and, in 1912, became Manager to the Taman Peninsular Oil Syndicate Ltd. In 1915 he went to Trinidad as Manager to Trinidad United Oilfields Ltd., and in 1917 was appointed Drilling and Production Superintendent to United British Oilfields of Trinidad Ltd.

Returning to England in 1920 Mr. Cherry was for a time a Special Instructor in Drilling in the University of Birmingham and later became Chief Engineer of the Oilfield Department of Vickers Ltd. In 1931 he founded the English Drilling Equipment Co. Ltd., which he actively controlled until the middle of 1945, when ill-health rendered it necessary for him to curtail his active direction, although he remained as Chairman.

By his death at the early age of 58 the industry loses another pioneer and a man of charming personality.

ERRATA.

"The Application of Variance Analysis to Some Problems of Petroleum Technology."

Page 472, line 19. For "90 per cent" read "95 per cent".

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